

ATTORNEY'S DOCKET NUMBER

U.S. APPLICATION NO (If known, see 37 CFR 1.5)

10/069945

PRIORITY DATE CLAIMED
07 September 1999 (7.09.99)

TITLE OF INVENTION
Recovery of Zinc from Zinc Bearing Sulphide Minerals by Bioleaching and Electrowinning
APPLICANT(S) FOR DO/EO/US BASSON, Petrus, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is attached hereto.
 - b. ☒ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☒ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). Unexecuted Declaration
10. ☒ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☒ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

- a) PCT Published Application WO 01/18266 published 15 March 2001
b) International Search Report dated December 13, 2000
c) International Preliminary Examination Report mailed December 17, 2001

U.S. APPLICATION NO. (if known) 10/069945 INTERNATIONAL APPLICATION NO. PCT/ZA00/00160	ATTORNEY'S DOCKET NUMBER P.19477/MAJR
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21. ☒ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1)-(5)):

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **\$1040.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **\$890.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **\$740.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **\$710.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **\$100.00**

ENTER APPROPRIATE BASIC FEE AMOUNT =

CALCULATIONS PTO USE ONLY

\$ **890.00**

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☒ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).

\$ **130.00**

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	32 - 20 =	12	x \$18.00	\$ 216.00
Independent claims	2 - 3 =	0	x \$84.00	\$ 0.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$280.00	\$ 0.00

TOTAL OF ABOVE CALCULATIONS = \$ **1,236.00**

☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.

\$ **0.00**

SUBTOTAL = \$ **1,236.00**

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)).

\$ **0.00**

TOTAL NATIONAL FEE = \$ **1,236.00**

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **\$40.00** per property +

\$ **0.00**

TOTAL FEES ENCLOSED = \$ **1,236.00**

Amount to be refunded:	\$
charged:	\$

- a. ☒ A check in the amount of \$ 1,236.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 10-1213. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Jennifer P. Yancy
 Jones, Tullar & Cooper, P.C.
 P.O. Box 2266
 Eads Station
 Arlington, VA 22202

Jennifer P. Yancy
 SIGNATURE

Jennifer P. Yancy

NAME

47,003

REGISTRATION NUMBER

10/069945
Rec'd PCT/PTO 19 SEP 2002
#5

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:)
BASSON, et al.) Atty. Docket No. P.19477/MAJR
Application No.: TBA)
Filed: March 7, 2002)
For: RECOVERY OF ZINC FROM ZINC)
BEARING SULPHIDE MINERALS BY)
BIOLEACHING AND ELECTROWINNING)

SECOND PRELIMINARY AMENDMENT

Assistant Commissioner of Patents
Washington, DC 20231

Sir:

This is a Preliminary Amendment in the application filed herewith under 35 U.S.C. 371.

Please amend the above-identified application as follows:

IN THE SPECIFICATIONS:

Please cancel the specification of the subject patent application as filed. That specification corresponds to the specification of PCT/ZA00/00160, filed 5 September 2000, published as WO 01/18266 on 15 March 2001, in favor of the accompanying Substitute Specification. A marked-up copy of the specification, showing the changes made thereto to arrive at the Substitute Specification is enclosed for the Examiner's review.

IN THE CLAIMS:

Please cancel claims 1-49, all of the claims set forth in the specification of the application as filed and provided by WO 01/18266, without prejudice. Please also cancel claims 1-32 which were believed to be submitted to the PCT on 09/10/2001 and which appear in the International Preliminary Examination Report, printed 12-12-2001.

Please add new claims 50-81, as follows:

50. A method of recovering zinc from a zinc bearing sulphide mineral slurry which includes the steps of:

- (a) subjecting the slurry in a reactor to a bioleaching process at a temperature in excess of 40°C;
- (b) supplying a feed gas which contains in excess of 21% oxygen by volume, to the slurry;
- (c) controlling the dissolved oxygen concentration in the slurry at a level of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$ by controlling at least one of the following: the oxygen content of the feed gas, the supply of feed gas to the slurry; the rate of feed of slurry to the reactor; and
- (d) recovering zinc from a bioleach residue of the bioleaching process.

51. The method according to claim 50 further including removing copper from said bioleach residue before recovering zinc therefrom.

52. The method according to claim 50 further including removing iron from said bioleach residue before recovering zinc therefrom.

53. The method according to claim 52 further including precipitating the iron from said bioleach residue by adding limestone to the residue.

54. The method according to claim 50 further including subjecting said bioleach residue to a recovery process which includes zinc solvent extraction and zinc electrowinning to produce zinc metal cathodes.

55. The method according to claim 54 further including feeding oxygen generated during zinc electrowinning to said feed gas of step (b) or directly to said slurry.

56. The method according to claim 54 supplying raffinate, produced during the zinc solvent extraction, to at least one of the following: the bioleaching process of step (a), an external heap leach process, and a zinc oxide leach stage.

57. The method according to any one of claims 54 further including neutralizing acid in raffinate, produced during the zinc solvent extraction, to produce gypsum and carbon dioxide, and to precipitate co-leached iron.

58. The method according to claim 57 wherein the step of neutralizing is effected by adding limestone or zinc oxide ore or concentrate to the raffinate.

59. The method according to claim 57 further including supplying at least some of the carbon dioxide to said bioleaching process of step (a).

60. The method according to claim 50 further including subjecting said bioleach residue to zinc dust purification by precipitation and electrowinning to produce zinc metal cathodes.

61. The method according to claim 60 further including supplying spent electrolyte from the zinc electrowinning to at least one of the following: the bioleaching process of step (a), an external heap leach process, and a zinc oxide leach stage.

62. The method according to claim 60 further including feeding oxygen generated during zinc electrowinning to the feed gas of step (b), or directly to said slurry.

63. The method according to claim 60 further including neutralizing spent electrolyte, from the zinc electrowinning, to produce gypsum and carbon dioxide, and to precipitate co-leached iron.

64. The method according to claim 63 wherein said step of neutralizing is effected by adding limestone or zinc oxide ore or concentrate to the spent electrolyte.

65. The method according to claim 63 further including supplying at least some of the carbon dioxide to the bioleaching process of step (a).

66. The method according to claim 50 wherein said feed gas in step (b) contains in excess of 85% oxygen by volume.

67. The method according to claim 50 further including controlling a carbon content of said slurry.

68. The method according to claim 50 further including controlling a carbon dioxide content of said feed gas in a range of from 0.5% to 5.0% by volume.

69. The method according to claims 50 wherein the said bioleaching process is carried out at a temperature in a range of from 40°C to 100°C.

70. The method according to claim 69 wherein said bioleaching process is carried out at a temperature in a range of from 60°C to 85°C.

71. The method according to claim 50 further including bioleaching said slurry at a temperature of up to 45°C using mesophile microorganisms.

72. The method according to claim 22 wherein said microorganisms are selected from the genus group comprising *Acidithiobacillus*; *Thiobacillus*; *Leptosprillum*; *Ferromicrobium*; and *Acidiphilium*.

73. The method according to claim 72 wherein said microorganisms are selected from the group comprising *Acidithiobacillus caldus*; *Acidithiobacillus thiooxidans*; *Acidithiobacillus ferrooxidans*; *Acidithiobacillus acidophilus*; *Thiobacillus prosperus*; *Leptospirillum ferrooxidans*; *Ferromicrobium acidophilus*; and *Acidiphilium cryptum*.

74. The method according to claim 50 including bioleaching said slurry at a temperature of from 45°C to 60°C using moderate thermophile microorganisms.

75. The method according to claim 74 wherein said microorganisms are selected from the genus group comprising *Acidithiobacillus*; *Acidimicrobium*; *Sulfobacillus*; *Ferroplasma*; and *Alicyclobacillus*.

76. The method according to claim 75 wherein said microorganisms are selected from the group comprising *Acidithiobacillus caldus*; *Acidimicrobium ferrooxidans*; *Sulfobacillus acidophilus*; *Sulfobacillus disulfidooxidans*; *Sulfobacillus thermosulfidooxidans*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; and *Alicyclobacillus acidocaldrius*.

77. The method according to claim 70 further including bioleaching said slurry at a temperature of from 60°C to 85°C using thermophilic microorganisms.

78. The method according to claim 77 wherein said microorganisms are selected from the genusgroup comprising *Acidothermus*; *Sulfolobus*; *Metallosphaera*; *Acidianus*; *Ferroplasma*; *Thermoplasma*; and *Picrophilus*.

79. The method according to claim 78 wherein said microorganisms are selected from the group comprising *Sulfolobus metallicus*; *Sulfolobus acidocaldarius*; *Sulfolobus thermosulfidooxidans*; *Acidianus infernus*; *Metallosphaera sedula*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; *Thermoplasma volcanium*; and *Picrophilus oshimae*.

80. A plant for recovering zinc from a zinc bearing sulphide mineral slurry which includes a reactor vessel, a source which feeds a zinc bearing sulphide mineral slurry to the vessel wherein a bioleaching process is carried out at a temperature in excess of 40°C, an oxygen source which supplies oxygen in the form of oxygen enriched gas or substantially pure oxygen to the slurry, a device which measures the dissolved oxygen concentration in the slurry in the vessel, a control mechanism whereby, in response to the said measure of dissolved oxygen concentration, the supply of oxygen from the oxygen source to the slurry is controlled to achieve a dissolved oxygen concentration in the slurry at a level of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$, and a recovery system which recovers zinc from a bioleach residue from the reactor vessel.

81. The plant according to claim 80 wherein said reactor vessel is operated at a temperature in excess of 60°C.

IN THE ABSTRACT:

Please add the Abstract of the Disclosure as set forth on the separate accompanying sheet.

REMARKS

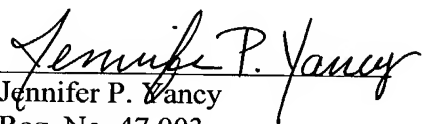
The specification of the subject patent application as filed has been canceled in favor of the accompanying Substitute Specification. The specification corresponds to the specification of PCT/ZA00/00160 filed 5 September 2000. This Substitute Specification generally places the specification in a form more in accordance with the U.S. practice. No new matter is added. A marked-up copy of the specification, which shows the changes made thereto to arrive at the substitute specification, is provided for the Examiner's review.

In accordance with my telephone conversation with Tamala D. Holland on September 19, 2002, claims 1-32 printed in the International Preliminary Examination Report dated 12/17/2001 have been canceled. Additionally, the original claims 1-49 in WO 01/18266 have been canceled in favor of new claims 50-81. These newly presented claims are similar to the claims added to the PCT application and have been written in a form more in accordance with U.S. practice and eliminating multiply dependent claims.

A suitable Abstract of the Disclosure has been added. This is generally similar to the Abstract set forth in the published application WO 01/18266. No new matter is being added.

Entry of this Preliminary Amendment prior to the examination of the application on its merits, and prior to the calculation of the filing fee is respectfully requested.

Respectfully submitted,


Jennifer P. Yancy
Reg. No. 47,003

JONES, TULLAR & COOPER, P.C.
P.O. Box 2266 Eads Station
Arlington, VA 22202
(703) 415-1500
September 19, 2002

Attorney Docket No. P.19477/MAJR

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:)
BASSON, et al.) Atty. Docket No. P.19477/MAJR
Application No.: TBA)
Filed: March 7, 2002)
For: RECOVERY OF ZINC FROM ZINC)
BEARING SULPHIDE MINERALS BY)
BIOLEACHING AND ELECTROWINNING)

PRELIMINARY AMENDMENT

Assistant Commissioner of Patents
Washington, DC 20231

Sir:

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IN THE SPECIFICATIONS:

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IN THE CLAIMS:

Please cancel claims 1-49, all of the claims set forth in the specification of the application as filed, without prejudice.

Please add new claims 50-81, as follows:

50. A method of recovering zinc from a zinc bearing sulphide mineral slurry which includes the steps of:

- (a) subjecting the slurry in a reactor to a bioleaching process at a temperature in excess of 40°C;
- (b) supplying a feed gas which contains in excess of 21% oxygen by volume, to the slurry;
- (c) controlling the dissolved oxygen concentration in the slurry at a level of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$ by controlling at least one of the following: the oxygen content of the feed gas, the supply of feed gas to the slurry; the rate of feed of slurry to the reactor; and
- (d) recovering zinc from a bioleach residue of the bioleaching process.

51. The method according to claim 50 further including removing copper from said bioleach residue before recovering zinc therefrom.

52. The method according to claim 50 further including removing iron from said bioleach residue before recovering zinc therefrom.

53. The method according to claim 52 further including precipitating the iron from said bioleach residue by adding limestone to the residue.

54. The method according to claim 50 further including subjecting said bioleach residue to a recovery process which includes zinc solvent extraction and zinc electrowinning to produce zinc metal cathodes.

55. The method according to claim 54 further including feeding oxygen generated during during zinc electrowinning to said feed gas of step (b) or directly to said slurry.

56. The method according to claim 54 supplying raffinate, produced during the zinc solvent extraction, to at least one of the following: the bioleaching process of step (a), an external heap leach process, and a zinc oxide leach stage.

57. The method according to any one of claims 54 further including neutralizing acid in raffinate, produced during the zinc solvent extraction, to produce gypsum and carbon dioxide, and to precipitate co-leached iron.

58. The method according to claim 57 wherein the step of neutralizing is effected by adding limestone or zinc oxide ore or concentrate to the raffinate.

59. The method according to claim 57 further including supplying at least some of the carbon dioxide to said bioleaching process of step (a).

60. The method according to claim 50 further including subjecting said bioleach residue to zinc dust purification by precipitation and electrowinning to produce zinc metal cathodes.

61. The method according to claim 60 further including supplying spent electrolyte from the zinc electrowinning to at least one of the following: the bioleaching process of step (a), an external heap leach process, and a zinc oxide leach stage.

62. The method according to claim 60 further including feeding oxygen generated during zinc electrowinning to the feed gas of step (b), or directly to said slurry.

63. The method according to claim 60 further including neutralizing spent electrolyte, from the zinc electrowinning, to produce gypsum and carbon dioxide, and to precipitate co-leached iron.

64. The method according to claim 63 wherein said step of neutralizing is effected by adding limestone or zinc oxide ore or concentrate to the spent electrolyte.

65. The method according to claim 63 further including supplying at least some of the carbon dioxide to the bioleaching process of step (a).

66. The method according to claim 50 wherein said feed gas in step (b) contains in excess of 85% oxygen by volume.

67. The method according to claim 50 further including controlling a carbon content of said slurry.

68. The method according to claim 50 further including controlling a carbon dioxide content of said feed gas in a range of from 0.5% to 5.0% by volume.

69. The method according to claims 50 wherein the said bioleaching process is carried out at a temperature in a range of from 40°C to 100°C.

70. The method according to claim 69 wherein said bioleaching process is carried out at a temperature in a range of from 60°C to 85°C.

71. The method according to claim 50 further including bioleaching said slurry at a temperature of up to 45°C using mesophile microorganisms.

72. The method according to claim 22 wherein said microorganisms are selected from the genus group comprising *Acidithiobacillus*; *Thiobacillus*; *Leptosprillum*; *Ferromicrobium*; and *Acidiphilium*.

73. The method according to claim 72 wherein said microorganisms are selected from the group comprising *Acidithiobacillus caldus*; *Acidithiobacillus thiooxidans*; *Acidithiobacillus ferrooxidans*; *Acidithiobacillus acidophilus*; *Thiobacillus prosperus*; *Leptospirillum ferrooxidans*; *Ferromicrobium acidophilus*; and *Acidiphilium cryptum*.

74. The method according to claim 50 including bioleaching said slurry at a temperature of from 45°C to 60°C using moderate thermophile microorganisms.

75. The method according to claim 74 wherein said microorganisms are selected from the genus group comprising *Acidithiobacillus*; *Acidimicrobium*; *Sulfobacillus*; *Ferroplasma*; and *Alicyclobacillus*.

76. The method according to claim 75 wherein said microorganisms are selected from the group comprising *Acidithiobacillus caldus*; *Acidimicrobium ferrooxidans*; *Sulfobacillus acidophilus*; *Sulfobacillus disulfidooxidans*; *Sulfobacillus thermosulfidooxidans*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; and *Alicyclobacillus acidocaldrius*.

77. The method according to claim 70 further including bioleaching said slurry at a temperature of from 60°C to 85°C using thermophilic microorganisms.

78. The method according to claim 77 wherein said microorganisms are selected from the genusgroup comprising *Acidothermus*; *Sulfolobus*; *Metallosphaera*; *Acidianus*; *Ferroplasma*; *Thermoplasma*; and *Picrophilus*.

79. The method according to claim 78 wherein said microorganisms are selected from the group comprising *Sulfolobus metallicus*; *Sulfolobus acidocaldarius*; *Sulfolobus thermosulfidooxidans*; *Acidianus infernus*; *Metallosphaera sedula*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; *Thermoplasma volcanium*; and *Picrophilus oshimae*.

80. A plant for recovering zinc from a zinc bearing sulphide mineral slurry which includes a reactor vessel, a source which feeds a zinc bearing sulphide mineral slurry to the vessel wherein a bioleaching process is carried out at a temperature in excess of 40°C, an oxygen source which supplies oxygen in the form of oxygen enriched gas or substantially pure oxygen to the slurry, a device which measures the dissolved oxygen concentration in the slurry in the vessel, a control mechanism whereby, in response to the said measure of dissolved oxygen concentration, the supply of oxygen from the oxygen source to the slurry is controlled to achieve a dissolved oxygen concentration in the slurry at a level of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$, and a recovery system which recovers zinc from a bioleach residue from the reactor vessel.

81. The plant according to claim 80 wherein said reactor vessel is operated at a temperature in excess of 60°C.

IN THE ABSTRACT:

Please add the Abstract of the Disclosure as set forth on the separate accompanying sheet.

REMARKS


The specification of the subject patent application as filed has been canceled in favor of the accompanying Substitute Specification. The specification corresponds to the specification of PCT/ZA00/00160 filed 5 September 2000. This Substitute Specification generally places the specification in a form more in accordance with the U.S. practice. No new matter is added. A marked-up copy of the specification, which shows the changes made thereto to arrive at the substitute specification, is provided for the Examiner's review.

Original claims 1-49 have been canceled in favor of new claims 50-81. These newly presented claims are similar to the claims added to the PCT application and have been written in a form more in accordance with U.S. practice and eliminating multiply dependent claims.

A suitable Abstract of the Disclosure has been added. This is generally similar to the Abstract set forth in the published application WO 01/18266. No new matter is being added.

Entry of this Preliminary Amendment prior to the examination of the application on its merits, and prior to the calculation of the filing fee is respectfully requested.

Respectfully submitted,


Jennifer P. Yancy
Reg. No. 47,003

JONES, TULLAR & COOPER, P.C.
P.O. Box 2266 Eads Station
Arlington, VA 22202
(703) 415-1500
March 7, 2002

Attorney Docket No. P.19477/MAJR

ABSTRACT OF THE DISCLOSURE

A method of recovering zinc from a zinc bearing sulphide mineral slurry which includes the steps of subjecting the slurry to a bioleaching process, supplying a feed gas which contains in excess of 21% oxygen by volume, to the slurry, and recovering zinc from a bioleach residue of the bioleaching process.

1
SUBSTITUTE SPECIFICATION – (Atty. Docket No. P.19477/MAJR)

RECOVERY OF ZINC FROM ZINC BEARING SULPHIDE MINERALS

RELATED APPLICATION

- 5 [001] This is a filing under 35 U.S.C. 371 of PCT/ZA00/00160, filed 5 September 2000, which claims priority from South African Application No. 99/5746, filed 7 September 1999. PCT/ZA00/00160 has been published under No. WO 01/18266, and the publication is in English.

BACKGROUND OF THE INVENTION

10

- [002] This invention relates to the recovery of zinc from zinc bearing sulphide minerals.

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- [003] Commercial bioleach plants which are currently in operation treating sulphide minerals, typically operate within the temperature range of 40°C to 50°C and rely on sparging air to the bioleach reactors to provide the required oxygen. Operation at this relatively low temperature and the use of air to supply oxygen, limit the rate of sulphide mineral oxidation that can be achieved.

20

- [004] The use of high temperatures between 50°C and 100°C greatly increases the rate of sulphide mineral leaching.

25

- [005] The solubility of oxygen is however limited at high temperatures and the rate of sulphide mineral leaching becomes limited. In the case of using air for the supply of oxygen, the effect of limited oxygen solubility is such that the rate of sulphide mineral leaching becomes dependent on and is limited by the rate of oxygen transfer from the gas to the liquid phase.

- [006] The bioleaching of zinc sulphide minerals is similarly problematic and to the applicant's knowledge no commercial zinc bioleaching plant is in operation.

SUMMARY OF THE INVENTION

[007] The invention provides a method of recovering zinc from a zinc bearing sulphide mineral slurry which

5 includes the steps of:

- (a) subjecting the slurry to a bioleaching process,
- (b) supplying a feed gas which contains in excess of 21% oxygen by volume, to the slurry, and
- (c) recovering zinc from a bioleach residue of the bioleaching process.

10 **[008]** If the slurry contains copper then preferably copper is removed from the bioleach residue before recovering zinc from the slurry.

[009] The method may include the step of removing iron from the bioleach residue before recovering zinc therefrom. This may be done in any appropriate way and preferably the iron is precipitated from the bioleach
15 residue by the addition of limestone to the slurry.

[010] Zinc may be extracted from the residue in any appropriate way. In one form of the invention the bioleach residue is subjected to a recovery process which includes solvent extraction and an electrowinning process to produce zinc metal cathodes.

20 **[011]** Oxygen generated during the zinc electrowinning step may be fed to the feed gas of step (b) or directly to the slurry.

[012] Raffinate produced during the solvent extraction step may be supplied to at least one of the following:
25 the bioleaching process of step (a), an external heap leach process, and a zinc oxide leach step.

[013] As used herein "zinc oxide" includes ores or concentrates containing non-sulphide zinc minerals.

[014] Acid in the raffinate may be neutralised to produce gypsum and carbon dioxide and to precipitate any co-leached iron.

[015] The neutralisation may be effected by adding limestone or zinc oxide to the raffinate.

5

[016] At least some of the carbon dioxide produced during the neutralisation step may be supplied to the bioleaching process of step (a).

[017] As used herein the expression "oxygen enriched gas" is intended to include a gas, e.g. air, which contains in excess of 21% oxygen by volume. This is an oxygen content greater than the oxygen content of air. The expression "pure oxygen" is intended to include a gas which contains in excess of 85% oxygen by volume. Preferably the feed gas which is supplied to the slurry contains in excess of 85% oxygen by volume i.e. is substantially pure oxygen.

[018] The method may include the step of maintaining the dissolved oxygen concentration in the slurry within a desired range which may be determined by the operating conditions and the type of microorganisms used for leaching. The applicant has established that a lower limit for the dissolved oxygen concentration to sustain microorganism growth and mineral oxidation, is in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. On the other hand if the dissolved oxygen concentration is too high then microorganism growth is inhibited. The upper threshold concentration also depends on the genus and strain of microorganism used in the leaching process and typically is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

[019] Thus, preferably, the dissolved oxygen concentration in the slurry is maintained in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

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[020] The method may include the steps of determining the dissolved oxygen concentration in the slurry and, in response thereto, of controlling at least one of the following: the oxygen content of the feed gas, the rate of supply of the feed gas to the slurry, and the rate of feed of slurry to a reactor.

[021] The dissolved oxygen concentration in the slurry may be determined in any appropriate way, e.g. by one or more of the following: by direct measurement of the dissolved oxygen concentration in the slurry, by measurement of the oxygen content in gas above the slurry, and indirectly by measurement of the oxygen content in off-gas from the slurry, taking into account the rate of oxygen supply, whether in gas enriched or pure form, to the slurry, and other relevant factors.

[022] The method may include the step of controlling the carbon content of the slurry. This may be achieved by one or more of the following: the addition of carbon dioxide gas to the slurry, and the addition of other carbonaceous material to the slurry.

[023] The method may extend to the step of controlling the carbon dioxide content of the feed gas to the slurry in the range of from 0.5% to 5% by volume. A suitable figure is of the order of 1% to 1.5% by volume. The level of the carbon dioxide is chosen to maintain high rates of microorganism growth and sulphide mineral oxidation.

[024] The bioleaching process is preferably carried out at an elevated temperature. As stated hereinbefore the bioleaching rate increases with an increase in operating temperature. Clearly the microorganisms which are used for bioleaching are determined by the operating temperature and vice versa. As the addition of oxygen enriched gas or substantially pure oxygen to the slurry has a cost factor it is desirable to operate at a temperature which increases the leaching rate by an amount which more than compensates for the increase in operating cost. Thus, preferably, the bioleaching is carried out at a temperature in excess of 40°C.

[025] The bioleaching may be carried out at a temperature of up to 100°C or more and preferably is carried out at a temperature which lies in a range of from 60°C to 85°C.

[026] In one form of the invention the method includes the step of bioleaching the slurry at a temperature of up to 45°C using mesophile microorganisms. These microorganisms may, for example, be selected from the following genus groups:

Acidithiobacillus (formerly *Thiobacillus*); *Leptosprillum*; *Ferromicrobium*; and *Acidiphilium*.

[027] In order to operate at this temperature the said microorganisms may, for example, be selected from the following species:

Acidithiobacillus caldus (*Thiobacillus caldus*); *Acidithiobacillus thiooxidans* (*Thiobacillus thiooxidans*);
 5 *Acidithiobacillus ferrooxidans* (*Thiobacillus ferrooxidans*); *Acidithiobacillus acidophilus* (*Thiobacillus acidophilus*); *Thiobacillus prosperus*; *Leptospirillum ferrooxidans*; *Ferromicrobium acidophilus*; and *Acidiphilium cryptum*.

[028] If the bioleaching step is carried out at a temperature of from 45°C to 60°C then moderate
 10 thermophile microorganisms may be used. These may, for example, be selected from the following genus groups:

Acidithiobacillus (formerly *Thiobacillus*); *Acidimicrobium*; *Sulfobacillus*; *Ferroplasma* (*Ferriplasma*); and *Alicyclobacillus*.

[029] Suitable moderate thermophile microorganisms may, for example, be selected from the following species:

Acidithiobacillus caldus (formerly *Thiobacillus caldus*); *Acidimicrobium ferrooxidans*; *Sulfobacillus acidophilus*; *Sulfobacillus disulfidooxidans*; *Sulfobacillus thermosulfidooxidans*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; and *Alicyclobacillus acidocaldrius*.

[030] It is preferred to operate the leaching process at a temperature in the range of from 60°C to 85°C using thermophilic microorganisms. These may, for example, be selected from the following genus groups:
 20 *Acidothermus*; *Sulfolobus*; *Metallosphaera*; *Acidianus*; *Ferroplasma* (*Ferriplasma*); *Thermoplasma*; and *Picrophilus*.

[031] Suitable thermophilic microorganisms may, for example, be selected from the following species:

Sulfolobus metallicus; *Sulfolobus acidocaldarius*; *Sulfolobus thermosulfidooxidans*; *Acidianus infernus*; *Metallosphaera sedula*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; *Thermoplasma volcanium*; and *Picrophilus oshimae*.

[032] The slurry may be leached in a reactor tank or vessel which is open to atmosphere or substantially closed. In the latter case vents for off-gas may be provided from the reactor.

5 **[033]** According to a different aspect of the invention there is provided a method of recovering zinc from a slurry containing zinc bearing sulphide minerals which includes the steps of bioleaching the slurry using suitable microorganisms at a temperature in excess of 40°C, controlling the dissolved oxygen concentration in the slurry within a predetermined range, and recovering zinc from a bioleach residue.

10 **[034]** Preferably the bioleaching is carried out at a temperature in excess of 60°C.

[035] The dissolved oxygen concentration may be controlled by controlling the addition of gas which contains in excess of 21% oxygen by volume to the slurry.

15 **[036]** Preferably the gas contains in excess of 85% oxygen by volume.

[037] The bioleach residue may be subjected to a separation step to produce residue solids and solution, and the zinc may be recovered from the solution in any appropriate way.

20 **[038]** The invention also extends to a method of enhancing the oxygen mass transfer coefficient from a gas phase to a liquid phase in a zinc bearing sulphide slurry which includes the step of supplying a feed gas containing in excess of 21% oxygen by volume to the slurry.

[039] The invention further extends to a plant for recovering zinc from a zinc bearing sulphide mineral
25 slurry which includes a reactor vessel, a source which feeds a zinc bearing sulphide mineral slurry to the vessel, an oxygen source, a device which measures the dissolved oxygen concentration in the slurry in the vessel, a control mechanism whereby, in response to the said measure of dissolved oxygen concentration, the supply of oxygen from the oxygen source to the slurry is controlled to achieve a dissolved oxygen

concentration in the slurry within a predetermined range, and a recovery system which recovers zinc from a bioleach residue from the reactor vessel.

5 **[040]** The said dissolved oxygen concentration may be controlled by controlling the supply of oxygen to the slurry.

[041] The oxygen may be supplied to the slurry in the form of oxygen enriched gas or substantially pure oxygen.

10 **[042]** The reactor vessel may be operated at a temperature in excess of 60°C and preferably in the range of 60°C to 85°C.

15 **[043]** The invention further extends to a method of bioleaching an aqueous slurry containing zinc sulphide minerals which includes the steps of bioleaching the slurry at a temperature above 60°C, and maintaining the dissolved oxygen concentration in the slurry in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

20 **[044]** Various techniques may be used for controlling the supply of oxygen to the slurry and hence for controlling the dissolved oxygen concentration in the slurry at a desired value. Use may for example be made of valves which are operated manually. For more accurate control use may be made of an automatic control system. These techniques are known in the art and are not further described herein.

25 **[045]** As has been indicated oxygen and carbon dioxide may be added to the slurry in accordance with predetermined criteria. Although the addition of these materials may be based on expected demand and measurement of other performance parameters, such as iron(II) concentration, it is preferred to make use of suitable measurement probes to sample the actual values of the critical parameters.

[046] For example use may be made of a dissolved oxygen probe to measure the dissolved oxygen concentration in the slurry directly. To achieve this the probe is immersed in the slurry. The dissolved oxygen concentration may be measured indirectly by using a probe in the reactor off-gas or by transmitting a

sample of the off-gas, at regular intervals, to an oxygen gas analyser. Again it is pointed out that measuring techniques of this type are known in the art and accordingly any appropriate technique can be used.

[047] A preferred approach to the control aspect is to utilise one or more probes to measure the dissolved oxygen concentration in the slurry, whether directly or indirectly. The probes produce one or more control signals which are used to control the operation of a suitable valve or valves, e.g. solenoid valves, automatically so that the supply of oxygen to an air stream which is being fed to the slurry is varied automatically in accordance with real time measurements of the dissolved oxygen concentration in the slurry

[048] Although it is preferred to control the addition of oxygen to a gas stream which is fed to the slurry a reverse approach may be adopted in that the oxygen supply rate to the reactor vessel may be maintained substantially constant and the rate of supply of the sulphide mineral slurry to the reactor vessel may be varied to achieve a desired dissolved oxygen concentration.

[049] The invention is not limited to the actual control technique employed and is intended to extend to variations of the foregoing approaches and to any equivalent process.

[050] Sphalerite, a commonly occurring zinc sulphide mineral, is of particular benefit, because it has a high leaching rate, even at typical mesophile operating temperatures, which is further increased at the higher temperatures used with moderate and extreme thermophiles. Thus the benefits of the invention, including a high specific reactor sulphide oxidation duty and reduced specific power requirement for oxidation, are obtained during the bioleaching of zinc bearing sulphide concentrates, even at mesophile operating temperatures.

[051] Bioleaching fixes the sulphur in the sulphide concentrate ultimately as gypsum, rather than as sulphuric acid in conventional processes. Thus there always exists the need to fix sulphur as gypsum. If oxide zinc bearing ore or concentrates are available, they usually have a significant carbonate related gangue acid requirement. The gangue acid requirement can therefore be used to fix sulphur as gypsum, simultaneously solubilising the zinc content, reducing or eliminating the need for additional sulphuric acid for

the treatment of these zinc oxide materials. For example a zinc oxide ore with a gangue acid consumption of 200kg sulphuric acid per tonne of ore could be processed using the acid generated from a zinc sulphide bioleach. If only 50% of the zinc oxide ore sulphuric acid requirement were to be met in this way, a 1 million tonnes per annum oxide leach would save US\$5 million per annum at a sulphuric acid price of US\$50 per tonne. The dilute sulphuric acid used for leaching of these zinc oxide materials would come either from a solvent extraction raffinate or from spent electrolyte, depending on the route chosen for zinc recovery.

[052] Zinc may be recovered from solution by any appropriate process, for example by direct electrowinning, (after purification of the solution by zinc dust precipitation), by solvent extraction or by resin-in-pulp (applied to the slurry), followed by electrowinning.

[053] If electrowinning is selected as the production method for zinc, the oxygen generated at the anode in the electrowinning process may be used to supplement that used in the bioleach process, reducing the capital and operating costs required for oxygen production.

BRIEF DESCRIPTION OF THE DRAWINGS

[054] The invention is further described by way of example with reference to the accompanying drawings in which:

[055] Figure 1 is a schematic representation of a portion of a plant in which the invention is carried out,

[056] Figures 2 to 4 show various results and parameters obtained from operating a bioreactor in the manner described herein with reference to Figure 1,

[057] Figure 5 is a flow chart of a zinc recovery process according to the invention, and

[058] Figure 6 illustrates a variation to the process shown in Figure 5.

DESCRIPTION OF PREFERRED EMBODIMENT

General Principles

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[059] The limitation of low oxygen solubility during bioleaching, using air, at high temperatures, which in turn limits the rate of reaction, requires enrichment of the air with oxygen i.e. air with an oxygen content greater than 21% by volume, or the use of pure oxygen (defined as being greater than 85% oxygen by volume). The use of oxygen enriched air or pure oxygen overcomes the limited rate of reaction due to oxygen supply constraints, but has two major disadvantages:

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- a) the provision of oxygen enriched air or pure oxygen is expensive and requires a high utilisation (>60%) of the oxygen to warrant the additional expense; and
- b) if the oxygen level in solution becomes too high microorganism growth is prevented and sulphide mineral bioleaching stops .

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[060] Therefore, in order to realise the benefits of high rates of sulphide mineral leaching at high temperatures in commercial bioleaching plants, the drawbacks of requiring expensive oxygen and the risk of failure if the dissolved oxygen levels become too high must be overcome.

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[061] The bioleaching of sulphide minerals at an elevated temperature results in a high rate of sulphide mineral oxidation, but is dependent on the supply of oxygen and carbon dioxide to maintain high rates of sulphide mineral oxidation and of microorganism growth at adequate rates. The absorption of oxygen and carbon dioxide in the bioleaching reactor is limited, in each case, by the rate of mass transfer from the gas phase into the solution phase. For oxygen the rate of oxygen absorption is defined by equation (1) as follows:

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$$R = M \cdot (C^* - C_L) \quad (1)$$

where:

R = Oxygen demand as mass (kg) per unit volume (m^3) per unit time(s) ($kg/m^3/s$),

M = Oxygen mass transfer coefficient in reciprocal seconds (s^{-1}),

C^* = Saturated dissolved oxygen concentration as mass (kg) per unit volume (m^3) (kg/m^3), and

C_L = Dissolved oxygen concentration in solution as mass (kg) per unit volume (m^3) (kg/m^3).

[062] The factor $(C^* - C_L)$ is referred to as the oxygen driving force. A similar equation may be used to describe the rate of carbon dioxide supply to the solution. If the sulphide mineral oxidation rate is increased the oxygen demand increases proportionately. To meet a higher oxygen demand either the oxygen mass transfer coefficient (M) or the oxygen driving force $(C^* - C_L)$ must be increased.

[063] An increase in the oxygen mass transfer coefficient may be achieved by increasing the power input to the bioleach reactor mixer. This improves gas dispersion in the sulphide mineral slurry. With this approach, however, an increase in the oxygen mass transfer coefficient of, for example, 40% requires an increase in the power input to the mixer by a factor of as much as 200%, with a commensurate increase in operating costs.

[064] The oxygen driving force may be increased by increasing the saturated dissolved oxygen concentration C^* and reducing the dissolved oxygen content or concentration C_L .

[065] Microorganism population growth is limited or prevented if the dissolved oxygen concentration C^* reaches too high a level. A concentration level above $4 \times 10^{-3} \text{ kg/m}^3$ has been found to be detrimental to *Sulfolobus*-like strains. Certain *Acidithiobacillus* strains, however, have been found to be tolerant to dissolved oxygen concentrations of up to $10 \times 10^{-3} \text{ kg/m}^3$.

[066] The applicant has established that a lower limit for the dissolved oxygen concentration to sustain microorganism growth and mineral oxidation is in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. Thus, in order to provide an adequate, or optimum, supply of oxygen, the dissolved oxygen content or concentration in the sulphide mineral slurry must be monitored and, where appropriate, the addition of oxygen to the sulphide mineral slurry must be controlled in order to maintain the minimum dissolved oxygen concentration in solution at a value of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$.

[067] On the other hand the dissolved oxygen concentration must not exceed an upper threshold value at which microorganism growth is prevented. It is pointed out that the upper threshold concentration depends on the genus and strain of microorganism used in the bioleaching process. A typical upper threshold value is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

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[068] As has been previously indicated the rate of sulphide mineral oxidation, which can be achieved when operating at a relatively low temperature of the order of from 40°C to 55°C , is limited. In order to increase the rate of oxidation it is desirable to make use of thermophiles and to operate at temperatures in excess of 60°C . Any suitable microorganism capable of operating within this temperature range may be used. The optimum operating temperature is dependent on the genus and type of microorganism used. Thus moderate thermophiles of the type *Sulfobacillus* are suitable for operating at a temperature of up to 65°C . Thermophiles of the type *Sulfolobus* are suitable for operating at temperatures of from 60°C to at least 85°C . *Sulfolobus metallicus*, for example, shows optimal growth in the temperature range of from 65°C to 70°C .

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[069] The applicant has established that the operation of the bioleaching process, using a gas enriched with oxygen, or pure oxygen, as the oxidant, at elevated temperatures of from 40°C to 85°C :

increases the specific sulphide oxidation duty of the reactor considerably;

results in an unexpected and significantly enhanced oxygen mass transfer rate;

increases the oxygen utilisation, providing that the dissolved oxygen concentration is controlled above the

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point where microorganism growth and mineral oxidation are prevented and below the point at which microorganism growth is inhibited; and

the overall power required for the oxidation of sulphide minerals is significantly reduced.

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[070] The method of the invention represents a significant improvement compared to a bioleach operation carried out at a temperature of from 40°C to 45°C with air.

[071] The controlled addition of oxygen enriched air or pure oxygen directly into the bioreactor improves the oxygen utilisation efficiency. The oxygen utilisation for a conventional commercial bioleach plant (at least 100m^3 in volume) operating at from 40°C to 45°C with air may be expected to achieve a maximum oxygen

utilisation factor of from 40% to 50%. Consequently only 40% to 50% of the total mass of oxygen supplied to the bioleach plant is used to oxidise the sulphide minerals. With the method of the invention the oxygen utilisation is significantly higher, of the order of from 60% to 95%. The higher oxygen utilisation is achieved by controlled oxygen addition and results from the enhanced oxygen mass transfer rate and by operating at low dissolved oxygen concentrations in the solution phase.

[072] It will be appreciated that although high oxygen demand in bioleach reactors has come about primarily by the use of higher temperatures, rapidly leaching sulphide minerals at temperatures below 60°C, using mesophile or moderate thermophile microorganisms, will have similarly high oxygen demands. The method of the invention is therefore not restricted to suit thermophiles or extreme thermophiles, but also mesophile and moderate thermophile microorganisms.

[073] Another advantage of using air enriched with oxygen or pure oxygen is that the evaporation losses are reduced, because there is less inert gas removing water vapour from the top of the reactor. This is particularly important in areas where water is scarce or expensive.

[074] In carrying out the method of the invention the temperature of the slurry in the bioleach vessel or reactor may be controlled in any suitable way known in the art. In one example the bioleach reactor is insulated and heating takes place by means of energy which is released by the oxidation of sulphides. The temperature of the slurry is regulated using any suitable cooling system, for example an internal cooling system.

[075] Table 1 shows typical data for specific sulphide oxidation duty and oxygen utilisation, when bioleaching with air at 40°C to 45°C, in two commercial bioreactors, Plant A and Plant B respectively, (greater than 100m³ in volume).

Description	Units	Plant A	Plant B
Reactor temperature	°C	42	40
Reactor operating volume	m ³	47	896
Oxygen utilisation	%	37.9	43.6
Typical dissolved oxygen concentration	mg/l	2.5	2.7
Oxygen mass transfer coefficient	s ⁻¹	0.047	0.031
Specific oxygen demand	kg/m ³ /day	21.6	14.8
Specific sulphide oxidation duty	kg/m ³ /day	8.9	5.7
Specific power consumption per kg sulphide oxidised	kWh/kgS ²⁻	1.7	1.8

5 **[076]** At low temperatures (40°C – 50°C), with air as the inlet gas, which applies to the results for the commercial reactors, Plant A and Plant B, presented in Table 1, the oxygen utilisations achieved are expected and the oxygen mass transfer coefficients (M) correspond to the applicant's design value. The applicant has determined that if the method of the invention were to be applied to Plant A, the plant performance would be significantly increased, as indicated by the results presented in Table 2.

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	Units	Plant A – typical operation	Plant A - using the method of the invention
Reactor temperature	°C	42	77
Microbial type strain	-	<i>Acidithiobacillus</i>	<i>Sulfolobus</i>
Inlet gas oxygen content	% by volume	20.9	90.0
Oxygen utilisation	%	37.9	93.0
Typical dissolved oxygen concentration	mg/l	2.5	2.5
Specific oxygen demand	kg/m ³ /day	21.6	59.5

Specific sulphide oxidation duty	kg/m ³ /day	8.9	24.5
Specific power consumption per kg sulphide oxidised	kWh/kgS ²⁻	1.7	1.2

[077] The results clearly show the benefit of the invention in achieving higher rates of reaction by the combination of bioleaching at high temperature, adding oxygen enriched gas and by controlling the dissolved oxygen concentration to a predetermined low level (e.g. 0.2×10^{-3} kg/m³ to 4.0×10^{-3} kg/m³). The specific sulphide oxidation duty of the reactor is increased by almost threefold. Clearly the upper dissolved oxygen concentration should not be increased above a value at which microorganism growth is inhibited or stopped.

[078] Even though additional capital for the production of oxygen is required, the savings in reactor and other costs at least offset this additional expense. Additionally, the specific power consumption per kg sulphide oxidised is decreased by approximately one-third. In a plant oxidising 300 tonnes of sulphide per day, the power saving, assuming a power cost of US\$0.05 per kWh, would amount to US\$2.8 million per annum. The high oxygen utilisation and increased specific sulphide oxidation capacity of the reactor represent in combination a considerable improvement over conventional bioleaching practice conducted at lower temperatures, with oxygen supplied by air.

Bioleaching Plant

[079] Figure 1 of the accompanying drawings shows a bioleaching plant 10 in which bioleaching is carried out, in accordance with the principles of the invention.

[080] The plant 10 includes a bioreactor 12 with an agitator or mixer 14 which is driven by means of a motor and gearbox assembly 16.

[081] In use a tank or vessel 18 of the reactor contains a sulphide mineral slurry 20. An impeller 22 of the agitator is immersed in the slurry and is used for mixing the slurry in a manner which is known in the art.

[082] A probe 24 is immersed in the slurry and is used for measuring the dissolved oxygen concentration in the slurry. A second probe 26, inside the tank 18 above the surface level 28 of the slurry, is used for measuring the carbon dioxide content in the gas 30 above the slurry 20.

5 [083] An oxygen source 32, a carbon dioxide source 34 and an air source 36 are connected through respective control valves 38, 40 and 42 to a sparging system 44, positioned in a lower zone inside the tank 18, immersed in the slurry 20.

10 [084] The probe 24 is used to monitor the dissolved oxygen concentration in the sulphide mineral slurry 20 and provides a control signal to a control device 46. The control device controls the operation of the oxygen supply valve 38 in a manner which is known in the art but in accordance with the principles which are described herein in order to maintain a desired dissolved oxygen concentration in the slurry 20.

15 [085] The probe 26 measures the carbon dioxide content in the gas above the sulphide mineral slurry 20. The probe 26 provides a control signal to a control device 48 which, in turn, controls the operation of the valve 40 in order to control the addition of carbon dioxide from the source 34 to a gas stream flowing to the sparger 44.

20 [086] The air flow rate from the source 36 to the sparger 44 is controlled by means of the valve 42. Normally the valve is set to provide a more or less constant flow of air from the source 36 to the sparger and the additions of oxygen and carbon dioxide to the air stream are controlled by the valves 38 and 40 respectively. Although this is a preferred approach to adjusting the oxygen and carbon dioxide contents in the air flow to the sparger other techniques can be adopted. For example it is possible, although with a lower degree of preference, to adjust the air stream flow rate and to mix the adjustable air stream with a steady
25 supply of oxygen and a variable supply of carbon dioxide, or vice versa. Another possibility is to have two separate air stream flows to which are added oxygen and carbon dioxide respectively. Irrespective of the technique which is adopted the objective remains the same, namely to control the additions of oxygen and carbon dioxide to the slurry 20.

[087] Slurry 50 is fed from a slurry feed source 52 through a control valve 54 and through an inlet pipe 56 into the interior of the tank 18. The slurry feed rate may be maintained substantially constant, by appropriate adjustment of the valve 54, to ensure that slurry is supplied to the tank 18 at a rate which sustains an optimum leaching rate. The supplies of air, oxygen and carbon dioxide are then regulated, taking into account the substantially constant slurry feed rate, to achieve a desired dissolved oxygen concentration in the slurry 20 in the tank, and a desired carbon dioxide content in the gas 30 above the slurry. Although this is a preferred approach it is apparent that the slurry feed rate could be adjusted, in response to a signal from the probe 24, to achieve a desired dissolved oxygen concentration in the slurry. In other words the rate of oxygen addition to the slurry may be kept substantially constant and the slurry feed rate may be varied according to requirement.

[088] Another variation which can be adopted is to move the probe 24 from a position at which it is immersed in the slurry to a position designated 24A at which it is located in the gas 30 above the level 28. The probe then measures the oxygen contained in the gas above the slurry i.e. the bioreactor off-gas. The oxygen content in the off-gas can also be used as a measure to control the dissolved oxygen concentration in the slurry, taking any other relevant factors into account.

[089] Conversely it may be possible to move the carbon dioxide probe 26 (provided it is capable of measuring the dissolved carbon dioxide content) from a position at which it is directly exposed to the gas 30 to a position designated 26A at which it is immersed in the slurry in the tank. The signal produced by the probe at the position 26A is then used, via the control device 48, to control the addition of carbon dioxide from the source 34 to the air stream from the source 36.

[090] Although the carbon dioxide source 34, which provides carbon dioxide in gas form, is readily controllable and represents a preferred way of introducing carbon into the slurry 20, it is possible to add suitable carbonate materials to the slurry 50 before feeding the slurry to the reactor. Carbonate material may also be added directly to the sulphide mineral slurry 20 in the reactor. In other cases though there may be sufficient carbonate in the sulphide mineral slurry so that it is not necessary to add carbon, in whatever form, to the slurry nor to control the carbon content in the slurry.

[091] It is apparent from the foregoing description which relates to the general principles of the invention that the supply of oxygen to the slurry is monitored and controlled to provide a desired dissolved oxygen concentration level in the slurry 20. This can be done in a variety of ways e.g. by controlling one or more of the following in an appropriate manner namely: the slurry feed rate, the air flow rate from the source 36, the oxygen flow rate from the source 32, and any variation of the foregoing.

[092] The carbon dioxide flow rate is changed in accordance with the total gas flow rate to the sparger 44 in order to maintain a concentration in the gas phase, i.e. in the gas stream to the reactor, of from 0.5% to 5% carbon dioxide by volume. This carbon dioxide range has been found to maintain an adequate dissolved carbon dioxide concentration in the slurry, a factor which is important in achieving effective leaching.

[093] The addition of oxygen to the sulphide mineral slurry 20 is controlled in order to maintain the minimum dissolved oxygen concentration in solution at a value of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. The upper threshold value depends on the genus and strain of microorganism used in the bioleaching process and typically is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

[094] Figure 1 illustrates the addition of oxygen from a source 32 of pure oxygen. The pure oxygen can be mixed with air from the source 36. Any other suitable gas can be used in place of the air. The addition of oxygen to air results to what is referred to in this specification as oxygen enriched gas i.e. a gas with an oxygen content in excess of 21% by volume. It is possible though to add oxygen substantially in pure form directly to the slurry. As used herein pure oxygen is intended to mean a gas stream which contains more than 85% oxygen by volume.

[095] The temperature in the bioleach reactor or vessel may be controlled in any appropriate way using techniques which are known in the art. In one example the tank 18 is insulated and heating takes place by means of energy which is released by the oxidation of sulphides. The temperature of the slurry 20 is regulated using an internal cooling system 70 which includes a plurality of heat exchanger cooling coils 72 connected to an external heat exchanger 74.

[096] The vessel 18 may be substantially sealed by means of a lid 80. Small vents 82 are provided to allow for the escape of off-gas. The off-gas may, if required, be captured or treated in any appropriate way before being released to atmosphere. Alternatively, according to requirement, the tank 18 may be open to atmosphere.

[097] The microorganisms chosen for the leaching process will determine the leaching temperature, and vice versa. The applicant has found that a preferred operating temperature is above 60°C, for example in the range of 60°C to 85°C. In this range thermophilic microorganisms, in any appropriate combination, are employed. In the range of from 45°C to 60°C, on the other hand, moderate thermophiles are employed while at temperatures below 45°C mesophiles are used. These microorganisms may, for example, be chosen from those referred to hereinbefore.

[098] Although the benefit of adding oxygen to the slurry which is to be leached, by making use of oxygen enriched air or, more preferably, by making use of substantially pure oxygen i.e. with an oxygen content in excess of 85%, is most pronounced at high temperatures at which greater leaching rates are possible, a benefit is nonetheless to be seen when oxygen enriched air or substantially pure oxygen is added to the slurry at lower temperatures, of the order of 40°C or even lower. At these temperatures the leaching rates are slower than at elevated temperatures and although an improvement results from using oxygen enriched air the cost thereof is generally not warranted by the relatively small increase in leaching rate.

Test Results

[099] The importance of maintaining an adequate supply of oxygen and hence a sufficiently high dissolved oxygen concentration to sustain microorganism growth and mineral oxidation is shown in the results presented in Figure 2. If the dissolved oxygen concentration is allowed to drop below 1.5 ppm, and particularly below 1.0 ppm, biooxidation becomes unstable, which is indicated by higher iron(II) concentrations in solution, of greater than 2 g/l. At consistent levels of biooxidation, achieved by maintaining

a dissolved oxygen concentration above 1.5 ppm, in this experiment, iron(II) is rapidly oxidised to iron(III), and iron(II) concentrations remain generally below 1.0 g/l.

[100] The results presented in Figure 2 were obtained from operation of a first or primary reactor of a continuous pilot plant treating a chalcopyrite concentrate at a feed solids concentration of 10% by mass and a temperature of 77°C, with *Sulfolobus*-like archaea.

[101] The effect of increasing the oxygen content of the feed gas to a bioreactor and controlling the dissolved oxygen concentration, in accordance with the principles of the invention, was tested in an experiment using a 5m³ bioreactor which was operated with a continuous pyrite or blended pyrrhotite and pyrite flotation concentrate feed, at a temperature of about 77°C, using a mixed culture of *Sulfolobus*-like archaea and a solids density of 10% by mass. The carbon dioxide content in the bioleach inlet gas was controlled at a level of between 1 and 1.5 % by volume. The dissolved oxygen concentration was generally within the range $0.4 \times 10^{-3} \text{ kg/m}^3$ to $3.0 \times 10^{-3} \text{ kg/m}^3$. The results of the experiment are presented in Figure 3.

[102] From the graphs presented in Figure 3 it is clear that, when sparging with air (enriched with carbon dioxide: 20.7% oxygen and 1.0% carbon dioxide), the maximum oxygen demand (directly proportional to the sulphide oxidation duty) was limited to 11.3 kg/m³/day, since the dissolved oxygen concentration which was achievable using air only (i.e. not enriched with oxygen) was just sufficient to maintain microorganism growth.

[103] By controlling the oxygen content of the inlet gas, the oxygen addition rate, and the dissolved oxygen concentration in the slurry in the range of $0.4 \times 10^{-3} \text{ kg/m}^3$ to $3.0 \times 10^{-3} \text{ kg/m}^3$, the oxygen demand, i.e. the sulphide mineral oxidation rate, was increased dramatically. The dissolved oxygen concentration was controlled to a low value, but above the minimum limit for successful microorganism growth, so that the utilisation of oxygen was maximised. The results show the oxygen demand, or sulphide oxidation duty, was increased by over threefold. Thus by increasing the oxygen content in the inlet gas from 20.7% to a maximum of 90.8% the specific oxygen demand was increased from 11.3 kg/m³/day to 33.7 kg/m³/day. In addition, by controlling the dissolved oxygen concentration to a low value, but above the minimum value for sustained

microorganism growth, the oxygen utilisation was maximised. The oxygen utilisation showed a general increase with an increase in the oxygen content of the inlet gas from 29% (for an inlet gas oxygen content of 20.7%) to 91% (for inlet gas containing 85.5% oxygen).

- 5 **[104]** The high oxygen utilisations achieved of well over 60% are much better than expected. Analysis of the results indicates that the oxygen mass transfer coefficient (M), as defined by equation (1), is significantly and unexpectedly enhanced for operation of the bioreactor at a high temperature (77°C) and with a high oxygen content in the inlet gas (from 29% to 91% in the experiment). In fact, the oxygen mass transfer coefficient (M) is increased by a factor of 2.69, on average, compared to the applicant's design value. This
- 10 enhancement is after considering the improvement in the mass transfer coefficient due to temperature, which would be expected to increase the value of M by a factor of 1.59 for a temperature increase from 42°C to 77°C , according to the temperature correction factor. This correction factor has been demonstrated experimentally to be valid for a temperature in the range of from 15°C to 70°C .
- 15 **[105]** The determination of the enhanced oxygen mass transfer coefficient is shown from the results presented in Figure 4, where the oxygen demand divided by the design oxygen mass transfer coefficient (M_{design}) is plotted against the oxygen driving force, as defined in equation (1). The slope of the regression line plotted through the data indicates the enhancement in the oxygen mass transfer coefficient by a factor of 2.69.

20

Process Example

- [106]** The inventive principles in the preceding section have been described in the context of sulphide minerals in general and, it will be appreciated by those skilled in the art, these principles can be applied in particular to zinc bearing sulphide minerals.
- 25

[107] Figure 5 of the accompanying drawings is a process flow chart illustrating the use of the method of the invention for recovering zinc.

[108] In Figure 5 the plant 10 which is shown in Figure 1 and which is described hereinbefore bears the same reference numeral. The oxygen, carbon dioxide and air sources bear the reference numerals 32, 34 and 36 respectively. The zinc bearing sulphide slurry is labelled with the numeral 50.

5

[109] The slurry 50 is fed to the plant 10 containing one or more bioleach reactors using oxygen enriched gas or pure oxygen, labelled 32, as the oxidant. The oxygen concentration in the reactor is controlled in the manner which has been described hereinbefore depending on the type of microorganism used.

10 **[110]** The bioleaching process produces a bioleach residue slurry 100 which contains solubilised zinc and iron, predominantly in the ferric state.

[111] Optionally at this point the bioleach residue slurry 100 may be subjected to a liquid/solid separation step 102 and copper 104, a metal commonly associated with zinc, can be recovered by solvent extraction
15 and electrowinning (106).

[112] Referring again to the main process flow stream iron in the bioleach residue slurry is removed by precipitation (108) brought about by the addition of limestone 110. The resulting slurry 112 is subjected to a liquid/solid separation step 114 producing solids 116 for disposal and a solution 118 which is fed to a zinc
20 solvent extraction step 120. The strip liquor 122 from the solvent extraction step 120 is obtained by stripping the loaded solvent with spent electrolyte 124 from a subsequent zinc electrowinning step 126 to produce zinc metal cathodes 128.

[113] Optionally raffinate 130 from the solvent extraction step 120 is used as a lixiviant for zinc oxide ore
25 132 (or concentrate if available) in an oxide leach stage 134. Some limestone 136 may be required to neutralise the acid in the raffinate, to produce gypsum and also to precipitate any co-leached iron and to produce carbon dioxide 140. The limestone will be required if the zinc oxide ore or concentrate 132 is not available.

[114] The oxide leach/acid neutralisation residue is subjected to a liquid/solid separation step 142 to produce solids 144 for disposal and a solution 146 which is fed to the zinc solvent extraction step 120.

[115] A portion of the raffinate 130 may optionally be recycled to the bioleach plant 10 to satisfy the acid requirement in the bioleaching reactor, or it may be directed to an external heap leach 148, where applicable.

[116] If there is insufficient carbonate in the slurry 50 then some of the carbon dioxide 140 generated in the neutralisation step may be added to the slurry, directly, or indirectly, for example by being blended with the oxygen enriched gas 32, or the carbon dioxide from the source 34, to provide the carbon dioxide requirement in the bioleaching phase.

[117] Oxygen gas 150 generated at the anode during the electrowinning step 126 may be recycled to supplement the oxygen requirement during the bioleaching step.

[118] Figure 6 illustrates a variation of the process shown in Figure 5. Steps in the process of Figure 6 which are the same as steps in the process of Figure 5 bear similar reference numerals. The following description relates only to the differences in the processes.

[119] If the solution 118 has a sufficiently high zinc concentration then, instead of using solvent extraction, the solution may be purified by using zinc dust precipitation.

[120] The solution 118 is fed to a purification step 200 in which zinc dust 202 is added to the solution. This causes the precipitation of impurities 204 in accordance with techniques which are known in the art and which consequently are not further described herein.

[121] The resulting purified solution 206 is fed to the electrowinning step 126. Spent electrolyte 124 is then used in the neutralisation step 134 (instead of the raffinate 130 in Figure 5). The spent electrolyte may also be recycled to the bioleach plant 10 or to the external heap leach 148.

[122] The solution 146, in the Figure 6 embodiment, is added to the solution from the solid/liquid separation step 114 to make up the solution 118.

Particular Example

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[123] Bioleach pilot plant test work was completed, using a sphalerite concentrate assaying 52% zinc, on a pilot plant of approximately 1.1 m³ consisting of 6 reactors configured as 2 primary reactors in parallel followed by 4 secondary reactors in series. The total primary volume was 470l and the total secondary volume was 630l. All test work was carried out at 77°C to 80°C using a zinc bearing sulphide feed slurry containing 7.5% solids. Microorganisms used were a mixed *Sulfolobus*-like archaea. Substantially pure oxygen was fed to the slurry. The oxygen utilisation results obtained in the primary stage during the test work, using analysis of inlet and outlet gas mixtures, are shown in Table 3.

10

Table 3 : Primary Reactor Zinc Dissolution and Oxygen Uptake Results for Thermophile Pilot Test Work

15

Retention Days	Zn Dissolution %	Specific Zn Dissolution Rate kg/m ³ /h	Oxygen Uptake (calculated) kg/m ³ /h	Oxygen Uptake (measured) kg/m ³ /h
1.8	90.4	0.865	0.847	0.856
1.5	88.0	1.010	0.989	0.915

[124] The results in Table 3 may be compared to mesophile results obtained at 40°C to 45°C, as reported in the literature. The test work was completed using a sphalerite concentrate containing 48.6% zinc at a similar grind size. The test results are shown in Table 4. Percentage zinc dissolution and oxygen uptakes were not reported, but were calculated using the specific zinc dissolution rate, assuming all zinc was in the form of sphalerite.

20

Table 4 : Primary Reactor Zinc Dissolution and Oxygen Uptake Results for Mesophile Bioleaching

Solids Content %	Retention Days	Zn Dissolution %	Specific Zn Dissolution Rate kg/m ³ /h	Oxygen Uptake (calculated) kg/m ³ /h
6.7	1.5	55.5	0.42	0.411
12.4	2.1	49.8	0.60	0.587

- [125] The results indicate that the oxygen uptake rate and hence the bioleaching rate may be enhanced by a factor of up to 1.5 to 2 by feeding oxygen enriched air or substantially pure oxygen to the slurry under controlled conditions.

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MARKED-UP COPY OF SPECIFICATION (Atty. Docket # P.19477/MAJR)

RECOVERY OF ZINC FROM ZINC BEARING SULPHIDE MINERALS

BACKGROUND OF THE INVENTION

- 5 This invention relates to the recovery of zinc from zinc bearing sulphide minerals.

Commercial bioleach plants which are currently in operation treating sulphide minerals, typically operate within the temperature range of 40°C to 50°C and rely on sparging air to the bioleach reactors to provide the required oxygen. Operation at this relatively low temperature and the use of air to supply oxygen, limit the
10 rate of sulphide mineral oxidation that can be achieved.

The use of high temperatures between 50°C and 100°C greatly increases the rate of sulphide mineral leaching.

- 15 The solubility of oxygen is however limited at high temperatures and the rate of sulphide mineral leaching becomes limited. In the case of using air for the supply of oxygen, the effect of limited oxygen solubility is such that the rate of sulphide mineral leaching becomes dependent on and is limited by the rate of oxygen transfer from the gas to the liquid phase^[(1,2)].

- 20 The bioleaching of zinc sulphide minerals is similarly problematic and to the applicant's knowledge no commercial zinc bioleaching plant is in operation.

SUMMARY OF THE INVENTION

- 25 The invention provides a method of recovering zinc from a zinc bearing sulphide mineral slurry which includes the steps of:
- (a) subjecting the slurry to a bioleaching process,
 - (b) supplying a feed gas which contains in excess of 21% oxygen by volume, to the slurry, and
 - (c) recovering zinc from a bioleach residue of the bioleaching process.

If the slurry contains copper then preferably copper is removed from the bioleach residue before recovering zinc from the slurry.

The method may include the step of removing iron from the bioleach residue before recovering zinc therefrom. This may be done in any appropriate way and preferably the iron is precipitated from the bioleach residue by the addition of limestone to the slurry.

Zinc may be extracted from the residue in any appropriate way. In one form of the invention the bioleach residue is subjected to a recovery process which includes solvent extraction and an electrowinning process to produce zinc metal cathodes.

Oxygen generated during the zinc electrowinning step may be fed to the feed gas of step (b) or directly to the slurry.

Raffinate produced during the solvent extraction step may be supplied to at least one of the following: the bioleaching process of step (a), an external heap leach process, and a zinc oxide leach step.

As used herein "zinc oxide" includes ores or concentrates containing non-sulphide zinc minerals.

Acid in the raffinate may be neutralised to produce gypsum and carbon dioxide and to precipitate any co-leached iron.

The neutralisation may be effected by adding limestone or zinc oxide to the raffinate.

At least some of the carbon dioxide produced during the neutralisation step may be supplied to the bioleaching process of step (a).

As used herein the expression "oxygen enriched gas" is intended to include a gas, e.g. air, which contains in excess of 21% oxygen by volume. This is an oxygen content greater than the oxygen content of air. The expression "pure oxygen" is intended to include a gas which contains in excess of 85% oxygen by volume. Preferably the feed gas which is supplied to the slurry contains in excess of 85% oxygen by volume i.e. is substantially pure oxygen.

The method may include the step of maintaining the dissolved oxygen concentration in the slurry within a desired range which may be determined by the operating conditions and the type of microorganisms used for leaching. The applicant has established that a lower limit for the dissolved oxygen concentration to sustain microorganism growth and mineral oxidation, is in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. On the other hand if the dissolved oxygen concentration is too high then microorganism growth is inhibited. The upper threshold concentration also depends on the genus and strain of microorganism used in the leaching process and typically is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

Thus, preferably, the dissolved oxygen concentration in the slurry is maintained in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

The method may include the steps of determining the dissolved oxygen concentration in the slurry and, in response thereto, of controlling at least one of the following: the oxygen content of the feed gas, the rate of supply of the feed gas to the slurry, and the rate of feed of slurry to a reactor.

The dissolved oxygen concentration in the slurry may be determined in any appropriate way, e.g. by one or more of the following: by direct measurement of the dissolved oxygen concentration in the slurry, by measurement of the oxygen content in gas above the slurry, and indirectly by measurement of the oxygen content in off-gas from the slurry, taking into account the rate of oxygen supply, whether in gas enriched or pure form, to the slurry, and other relevant factors.

The method may include the step of controlling the carbon content of the slurry. This may be achieved by one or more of the following: the addition of carbon dioxide gas to the slurry, and the addition of other carbonaceous material to the slurry.

- 5 The method may extend to the step of controlling the carbon dioxide content of the feed gas to the slurry in the range of from 0.5% to 5% by volume. A suitable figure is of the order of 1% to 1.5% by volume. The level of the carbon dioxide is chosen to maintain high rates of microorganism growth and sulphide mineral oxidation.
- 10 The bioleaching process is preferably carried out at an elevated temperature. As stated hereinbefore the bioleaching rate increases with an increase in operating temperature. Clearly the microorganisms which are used for bioleaching are determined by the operating temperature and vice versa. As the addition of oxygen enriched gas or substantially pure oxygen to the slurry has a cost factor it is desirable to operate at a temperature which increases the leaching rate by an amount which more than compensates for the increase
- 15 in operating cost. Thus, preferably, the bioleaching is carried out at a temperature in excess of 40°C.

The bioleaching may be carried out at a temperature of up to 100°C or more and preferably is carried out at a temperature which lies in a range of from 60°C to 85°C.

- 20 In one form of the invention the method includes the step of bioleaching the slurry at a temperature of up to 45°C using mesophile microorganisms. These microorganisms may, for example, be selected from the following genus groups:

Acidithiobacillus (formerly *Thiobacillus*); *Leptosprillum*; *Ferromicrobium*; and *Acidiphilium*.

- 25 In order to operate at this temperature the said microorganisms may, for example, be selected from the following species:

Acidithiobacillus caldus (*Thiobacillus caldus*); *Acidithiobacillus thiooxidans* (*Thiobacillus thiooxidans*); *Acidithiobacillus ferrooxidans* (*Thiobacillus ferrooxidans*); *Acidithiobacillus acidophilus* (*Thiobacillus*

acidophilus); *Thiobacillus prosperus*; *Leptospirillum ferrooxidans*; *Ferromicrobium acidophilus*; and *Acidiphilium cryptum*.

If the bioleaching step is carried out at a temperature of from 45°C to 60°C then moderate thermophile

5 microorganisms may be used. These may, for example, be selected from the following genus groups:

Acidithiobacillus (formerly *Thiobacillus*); *Acidimicrobium*; *Sulfobacillus*; *Ferroplasma* (*Ferriplasma*); and *Alicyclobacillus*.

Suitable moderate thermophile microorganisms may, for example, be selected from the following species:

10 *Acidithiobacillus caldus* (formerly *Thiobacillus caldus*); *Acidimicrobium ferrooxidans*; *Sulfobacillus acidophilus*; *Sulfobacillus disulfidooxidans*; *Sulfobacillus thermosulfidooxidans*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; and *Alicyclobacillus acidocaldrius*.

It is preferred to operate the leaching process at a temperature in the range of from 60°C to 85°C using

15 thermophilic microorganisms. These may, for example, be selected from the following genus groups:

Acidothermus; *Sulfolobus*; *Metallosphaera*; *Acidianus*; *Ferroplasma* (*Ferriplasma*); *Thermoplasma*; and *Picrophilus*.

Suitable thermophilic microorganisms may, for example, be selected from the following species:

20 *Sulfolobus metallicus*; *Sulfolobus acidocaldarius*; *Sulfolobus thermosulfidooxidans*; *Acidianus infernus*, *Metallosphaera sedula*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; *Thermoplasma volcanium*; and *Picrophilus oshimae*.

The slurry may be leached in a reactor tank or vessel which is open to atmosphere or substantially closed. In

25 the latter case vents for off-gas may be provided from the reactor.

According to a different aspect of the invention there is provided a method of recovering zinc from a slurry containing zinc bearing sulphide minerals which includes the steps of bioleaching the slurry using suitable

microorganisms at a temperature in excess of 40°C, controlling the dissolved oxygen concentration in the slurry within a predetermined range, and recovering zinc from a bioleach residue.

Preferably the bioleaching is carried out at a temperature in excess of 60°C.

5

The dissolved oxygen concentration may be controlled by controlling the addition of gas which contains in excess of 21% oxygen by volume to the slurry.

Preferably the gas contains in excess of 85% oxygen by volume.

10

The bioleach residue may be subjected to a separation step to produce residue solids and solution, and the zinc may be recovered from the solution in any appropriate way.

15

The invention also extends to a method of enhancing the oxygen mass transfer coefficient from a gas phase to a liquid phase in a zinc bearing sulphide slurry which includes the step of supplying a feed gas containing in excess of 21% oxygen by volume to the slurry.

20

The invention further extends to a plant for recovering zinc from a zinc bearing sulphide mineral slurry which includes a reactor vessel, a source which feeds a zinc bearing sulphide mineral slurry to the vessel, an oxygen source, a device which measures the dissolved oxygen concentration in the slurry in the vessel, a control mechanism whereby, in response to the said measure of dissolved oxygen concentration, the supply of oxygen from the oxygen source to the slurry is controlled to achieve a dissolved oxygen concentration in the slurry within a predetermined range, and a recovery system which recovers zinc from a bioleach residue from the reactor vessel.

25

The said dissolved oxygen concentration may be controlled by controlling the supply of oxygen to the slurry.

The oxygen may be supplied to the slurry in the form of oxygen enriched gas or substantially pure oxygen.

The reactor vessel may be operated at a temperature in excess of 60°C and preferably in the range of 60°C to 85°C.

The invention further extends to a method of bioleaching an aqueous slurry containing zinc sulphide minerals which includes the steps of bioleaching the slurry at a temperature above 60°C, and maintaining the dissolved oxygen concentration in the slurry in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

Various techniques may be used for controlling the supply of oxygen to the slurry and hence for controlling the dissolved oxygen concentration in the slurry at a desired value. Use may for example be made of valves which are operated manually. For more accurate control use may be made of an automatic control system. These techniques are known in the art and are not further described herein.

As has been indicated oxygen and carbon dioxide may be added to the slurry in accordance with predetermined criteria. Although the addition of these materials may be based on expected demand and measurement of other performance parameters, such as iron(II) concentration, it is preferred to make use of suitable measurement probes to sample the actual values of the critical parameters.

For example use may be made of a dissolved oxygen probe to measure the dissolved oxygen concentration in the slurry directly. To achieve this the probe is immersed in the slurry. The dissolved oxygen concentration may be measured indirectly by using a probe in the reactor off-gas or by transmitting a sample of the off-gas, at regular intervals, to an oxygen gas analyser. Again it is pointed out that measuring techniques of this type are known in the art and accordingly any appropriate technique can be used.

A preferred approach to the control aspect is to utilise one or more probes to measure the dissolved oxygen concentration in the slurry, whether directly or indirectly. The probes produce one or more control signals which are used to control the operation of a suitable valve or valves, e.g. solenoid valves, automatically so that the supply of oxygen to an air stream which is being fed to the slurry is varied automatically in accordance with real time measurements of the dissolved oxygen concentration in the slurry

Although it is preferred to control the addition of oxygen to a gas stream which is fed to the slurry a reverse approach may be adopted in that the oxygen supply rate to the reactor vessel may be maintained substantially constant and the rate of supply of the sulphide mineral slurry to the reactor vessel may be varied to achieve a desired dissolved oxygen concentration.

5

The invention is not limited to the actual control technique employed and is intended to extend to variations of the foregoing approaches and to any equivalent process.

10 Sphalerite, a commonly occurring zinc sulphide mineral, is of particular benefit, because it has a high leaching rate, even at typical mesophile operating temperatures, which is further increased at the higher temperatures used with moderate and extreme thermophiles. Thus the benefits of the invention, including a high specific reactor sulphide oxidation duty and reduced specific power requirement for oxidation, are obtained during the bioleaching of zinc bearing sulphide concentrates, even at mesophile operating temperatures.

15

Bioleaching fixes the sulphur in the sulphide concentrate ultimately as gypsum, rather than as sulphuric acid in conventional processes. Thus there always exists the need to fix sulphur as gypsum. If oxide zinc bearing ore or concentrates are available, they usually have a significant carbonate related gangue acid requirement. The gangue acid requirement can therefore be used to fix sulphur as gypsum, simultaneously solubilising the zinc content, reducing or eliminating the need for additional sulphuric acid for the treatment of these zinc oxide materials. For example a zinc oxide ore with a gangue acid consumption of 200kg sulphuric acid per tonne of ore could be processed using the acid generated from a zinc sulphide bioleach. If only 50% of the zinc oxide ore sulphuric acid requirement were to be met in this way, a 1 million tonnes per annum oxide leach would save US\$5 million per annum at a sulphuric acid price of US\$50 per tonne. The dilute sulphuric acid used for leaching of these zinc oxide materials would come either from a solvent extraction raffinate or from spent electrolyte, depending on the route chosen for zinc recovery.

20

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Zinc may be recovered from solution by any appropriate process, for example by direct electrowinning, (after purification of the solution by zinc dust precipitation), by solvent extraction or by resin-in-pulp (applied to the slurry), followed by electrowinning.

- 5 If electrowinning is selected as the production method for zinc, the oxygen generated at the anode in the electrowinning process may be used to supplement that used in the bioleach process, reducing the capital and operating costs required for oxygen production.

BRIEF DESCRIPTION OF THE DRAWINGS

10

The invention is further described by way of example with reference to the accompanying drawings in which:

Figure 1 is a schematic representation of a portion of a plant in which the invention is carried out,

Figures 2 to 4 show various results and parameters obtained from operating a bioreactor in the manner described herein with reference to Figure 1,

- 15 Figure 5 is a flow chart of a zinc recovery process according to the invention, and

Figure 6 illustrates a variation to the process shown in Figure 5.

DESCRIPTION OF PREFERRED EMBODIMENT

20 General Principles

The limitation of low oxygen solubility during bioleaching, using air, at high temperatures, which in turn limits the rate of reaction, requires enrichment of the air with oxygen i.e. air with an oxygen content greater than 21% by volume, or the use of pure oxygen (defined as being greater than 85% oxygen by volume). The use
25 of oxygen enriched air or pure oxygen overcomes the limited rate of reaction due to oxygen supply constraints, but has two major disadvantages:

- a) the provision of oxygen enriched air or pure oxygen is expensive and requires a high utilisation (>60%) of the oxygen to warrant the additional expense⁽³⁾, and

- b) if the oxygen level in solution becomes too high microorganism growth is prevented and sulphide mineral bioleaching stops⁽⁴⁾.

Therefore, in order to realise the benefits of high rates of sulphide mineral leaching at high temperatures in commercial bioleaching plants, the drawbacks of requiring expensive oxygen and the risk of failure if the dissolved oxygen levels become too high must be overcome.

The bioleaching of sulphide minerals at an elevated temperature results in a high rate of sulphide mineral oxidation, but is dependent on the supply of oxygen and carbon dioxide to maintain high rates of sulphide mineral oxidation and of microorganism growth at adequate rates. The absorption of oxygen and carbon dioxide in the bioleaching reactor is limited, in each case, by the rate of mass transfer from the gas phase into the solution phase. For oxygen the rate of oxygen absorption is defined by equation (1) as follows:

$$R = M \cdot (C^* - C_L) \quad (1)$$

where: R = Oxygen demand as mass (kg) per unit volume (m^3) per unit time(s) ($kg/m^3/s$),

M = Oxygen mass transfer coefficient in reciprocal seconds (s^{-1}),

C^* = Saturated dissolved oxygen concentration as mass (kg) per unit volume (m^3) (kg/m^3),

and

C_L = Dissolved oxygen concentration in solution as mass (kg) per unit volume (m^3) (kg/m^3).

The factor $(C^* - C_L)$ is referred to as the oxygen driving force. A similar equation may be used to describe the rate of carbon dioxide supply to the solution. If the sulphide mineral oxidation rate is increased the oxygen demand increases proportionately. To meet a higher oxygen demand either the oxygen mass transfer coefficient (M) or the oxygen driving force $(C^* - C_L)$ must be increased.

An increase in the oxygen mass transfer coefficient may be achieved by increasing the power input to the bioleach reactor mixer. This improves gas dispersion in the sulphide mineral slurry. With this approach, however, an increase in the oxygen mass transfer coefficient of, for example, 40% requires an increase in the power input to the mixer by a factor of as much as 200%, with a commensurate increase in operating costs.

The oxygen driving force may be increased by increasing the saturated dissolved oxygen concentration C^* and reducing the dissolved oxygen content or concentration C_L .

Microorganism population growth is limited or prevented if the dissolved oxygen concentration C^* reaches too high a level. A concentration level above $4 \times 10^{-3} \text{ kg/m}^3$ has been found to be detrimental to *Sulfolobus*-like strains. Certain *Acidithiobacillus* strains, however, have been found to be tolerant to dissolved oxygen concentrations of up to $10 \times 10^{-3} \text{ kg/m}^3$.

The applicant has established that a lower limit for the dissolved oxygen concentration to sustain microorganism growth and mineral oxidation is in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. Thus, in order to provide an adequate, or optimum, supply of oxygen, the dissolved oxygen content or concentration in the sulphide mineral slurry must be monitored and, where appropriate, the addition of oxygen to the sulphide mineral slurry must be controlled in order to maintain the minimum dissolved oxygen concentration in solution at a value of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$.

On the other hand the dissolved oxygen concentration must not exceed an upper threshold value at which microorganism growth is prevented. It is pointed out that the upper threshold concentration depends on the genus and strain of microorganism used in the bioleaching process. A typical upper threshold value is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

As has been previously indicated the rate of sulphide mineral oxidation, which can be achieved when operating at a relatively low temperature of the order of from 40°C to 55°C , is limited. In order to increase the rate of oxidation it is desirable to make use of thermophiles and to operate at temperatures in excess of 60°C . Any suitable microorganism capable of operating within this temperature range may be used. The optimum operating temperature is dependent on the genus and type of microorganism used. Thus moderate thermophiles of the type *Sulfobacillus* are suitable for operating at a temperature of up to 65°C . Thermophiles of the type *Sulfolobus* are suitable for operating at temperatures of from 60°C to at least 85°C . *Sulfolobus metallicus*, for example, shows optimal growth in the temperature range of from 65°C to 70°C .

The applicant has established that the operation of the bioleaching process, using a gas enriched with oxygen, or pure oxygen, as the oxidant, at elevated temperatures of from 40°C to 85°C:

increases the specific sulphide oxidation duty of the reactor considerably;

results in an unexpected and significantly enhanced oxygen mass transfer rate;

- 5 increases the oxygen utilisation, providing that the dissolved oxygen concentration is controlled above the point where microorganism growth and mineral oxidation are prevented and below the point at which microorganism growth is inhibited; and

the overall power required for the oxidation of sulphide minerals is significantly reduced.

- 10 The method of the invention represents a significant improvement compared to a bioleach operation carried out at a temperature of from 40°C to 45°C with air.

The controlled addition of oxygen enriched air or pure oxygen directly into the bioreactor improves the oxygen utilisation efficiency. The oxygen utilisation for a conventional commercial bioleach plant (at least 100m³ in
15 volume) operating at from 40°C to 45°C with air may be expected to achieve a maximum oxygen utilisation factor of from 40% to 50%. Consequently only 40% to 50% of the total mass of oxygen supplied to the bioleach plant is used to oxidise the sulphide minerals. With the method of the invention the oxygen utilisation is significantly higher, of the order of from 60% to 95%. The higher oxygen utilisation is achieved by controlled oxygen addition and results from the enhanced oxygen mass transfer rate and by operating at low
20 dissolved oxygen concentrations in the solution phase.

- It will be appreciated that although high oxygen demand in bioleach reactors has come about primarily by the use of higher temperatures, rapidly leaching sulphide minerals at temperatures below 60°C, using mesophile or moderate thermophile microorganisms, will have similarly high oxygen demands. The method of the
25 invention is therefore not restricted to suit thermophiles or extreme thermophiles, but also mesophile and moderate thermophile microorganisms.

Another advantage of using air enriched with oxygen or pure oxygen is that the evaporation losses are reduced, because there is less inert gas removing water vapour from the top of the reactor. This is particularly important in areas where water is scarce or expensive.

- 5 In carrying out the method of the invention the temperature of the slurry in the bioleach vessel or reactor may be controlled in any suitable way known in the art. In one example the bioleach reactor is insulated and heating takes place by means of energy which is released by the oxidation of sulphides. The temperature of the slurry is regulated using any suitable cooling system, for example an internal cooling system.
- 10 Table 1 shows typical data for specific sulphide oxidation duty and oxygen utilisation, when bioleaching with air at 40°C to 45°C, in two commercial bioreactors, Plant A and Plant B respectively, (greater than 100m³ in volume).

Table 1 Commercial Bioreactor Performance Results

15

Description	Units	Plant A	Plant B
Reactor temperature	°C	42	40
Reactor operating volume	m ³	471	896
Oxygen utilisation	%	37.9	43.6
Typical dissolved oxygen concentration	mg/l	2.5	2.7
Oxygen mass transfer coefficient	s ⁻¹	0.047	0.031
Specific oxygen demand	kg/m ³ /day	21.6	14.8
Specific sulphide oxidation duty	kg/m ³ /day	8.9	5.7
Specific power consumption per kg sulphide oxidised	kWh/kgS ²⁻	1.7	1.8

At low temperatures (40°C – 50°C), with air as the inlet gas, which applies to the results for the commercial reactors, Plant A and Plant B, presented in Table 1, the oxygen utilisations achieved are expected and the oxygen mass transfer coefficients (M) correspond to the applicant's design value. The applicant has

determined that if the method of the invention were to be applied to Plant A, the plant performance would be significantly increased, as indicated by the results presented in Table 2.

Table 2 Predicted Improvement In Commercial Bioreactor Performance

	Units	Plant A – typical operation	Plant A - using the method of the invention
Reactor temperature	°C	42	77
Microbial type strain	-	<i>Acidithiobacillus</i>	<i>Sulfolobus</i>
Inlet gas oxygen content	% by volume	20.9	90.0
Oxygen utilisation	%	37.9	93.0
Typical dissolved oxygen concentration	mg/l	2.5	2.5
Specific oxygen demand	kg/m ³ /day	21.6	59.5
Specific sulphide oxidation duty	kg/m ³ /day	8.9	24.5
Specific power consumption per kg sulphide oxidised	kWh/kgS ²⁻	1.7	1.2

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The results clearly show the benefit of the invention in achieving higher rates of reaction by the combination of bioleaching at high temperature, adding oxygen enriched gas and by controlling the dissolved oxygen concentration to a predetermined low level (e.g. $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$). The specific sulphide oxidation duty of the reactor is increased by almost threefold. Clearly the upper dissolved oxygen concentration should not be increased above a value at which microorganism growth is inhibited or stopped.

10

Even though additional capital for the production of oxygen is required, the savings in reactor and other costs at least offset this additional expense. Additionally, the specific power consumption per kg sulphide oxidised is decreased by approximately one-third. In a plant oxidising 300 tonnes of sulphide per day, the power saving, assuming a power cost of US\$0.05 per kWh, would amount to US\$2.8 million per annum. The high oxygen utilisation and increased specific sulphide oxidation capacity of the reactor represent in combination a considerable improvement over conventional bioleaching practice conducted at lower temperatures, with oxygen supplied by air.

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Bioleaching Plant

Figure 1 of the accompanying drawings shows a bioleaching plant 10 in which bioleaching is carried out, in accordance with the principles of the invention.

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The plant 10 includes a bioreactor 12 with an agitator or mixer 14 which is driven by means of a motor and gearbox assembly 16.

10

In use a tank or vessel 18 of the reactor contains a sulphide mineral slurry 20. An impeller 22 of the agitator is immersed in the slurry and is used for mixing the slurry in a manner which is known in the art.

A probe 24 is immersed in the slurry and is used for measuring the dissolved oxygen concentration in the slurry. A second probe 26, inside the tank 18 above the surface level 28 of the slurry, is used for measuring the carbon dioxide content in the gas 30 above the slurry 20.

15

An oxygen source 32, a carbon dioxide source 34 and an air source 36 are connected through respective control valves 38, 40 and 42 to a sparging system 44, positioned in a lower zone inside the tank 18, immersed in the slurry 20.

20

The probe 24 is used to monitor the dissolved oxygen concentration in the sulphide mineral slurry 20 and provides a control signal to a control device 46. The control device controls the operation of the oxygen supply valve 38 in a manner which is known in the art but in accordance with the principles which are described herein in order to maintain a desired dissolved oxygen concentration in the slurry 20.

25

The probe 26 measures the carbon dioxide content in the gas above the sulphide mineral slurry 20. The probe 26 provides a control signal to a control device 48 which, in turn, controls the operation of the valve 40 in order to control the addition of carbon dioxide from the source 34 to a gas stream flowing to the sparger 44.

The air flow rate from the source 36 to the sparger 44 is controlled by means of the valve 42. Normally the valve is set to provide a more or less constant flow of air from the source 36 to the sparger and the additions of oxygen and carbon dioxide to the air stream are controlled by the valves 38 and 40 respectively. Although this is a preferred approach to adjusting the oxygen and carbon dioxide contents in the air flow to the sparger other techniques can be adopted. For example it is possible, although with a lower degree of preference, to adjust the air stream flow rate and to mix the adjustable air stream with a steady supply of oxygen and a variable supply of carbon dioxide, or vice versa. Another possibility is to have two separate air stream flows to which are added oxygen and carbon dioxide respectively. Irrespective of the technique which is adopted the objective remains the same, namely to control the additions of oxygen and carbon dioxide to the slurry

Slurry 50 is fed from a slurry feed source 52 through a control valve 54 and through an inlet pipe 56 into the interior of the tank 18. The slurry feed rate may be maintained substantially constant, by appropriate adjustment of the valve 54, to ensure that slurry is supplied to the tank 18 at a rate which sustains an optimum leaching rate. The supplies of air, oxygen and carbon dioxide are then regulated, taking into account the substantially constant slurry feed rate, to achieve a desired dissolved oxygen concentration in the slurry 20 in the tank, and a desired carbon dioxide content in the gas 30 above the slurry. Although this is a preferred approach it is apparent that the slurry feed rate could be adjusted, in response to a signal from the probe 24, to achieve a desired dissolved oxygen concentration in the slurry. In other words the rate of oxygen addition to the slurry may be kept substantially constant and the slurry feed rate may be varied according to requirement.

Another variation which can be adopted is to move the probe 24 from a position at which it is immersed in the slurry to a position designated 24A at which it is located in the gas 30 above the level 28. The probe then measures the oxygen contained in the gas above the slurry i.e. the bioreactor off-gas. The oxygen content in the off-gas can also be used as a measure to control the dissolved oxygen concentration in the slurry, taking any other relevant factors into account.

Conversely it may be possible to move the carbon dioxide probe 26 (provided it is capable of measuring the dissolved carbon dioxide content) from a position at which it is directly exposed to the gas 30 to a position designated 26A at which it is immersed in the slurry in the tank. The signal produced by the probe at the position 26A is then used, via the control device 48, to control the addition of carbon dioxide from the source 34 to the air stream from the source 36.

Although the carbon dioxide source 34, which provides carbon dioxide in gas form, is readily controllable and represents a preferred way of introducing carbon into the slurry 20, it is possible to add suitable carbonate materials to the slurry 50 before feeding the slurry to the reactor. Carbonate material may also be added directly to the sulphide mineral slurry 20 in the reactor. In other cases though there may be sufficient carbonate in the sulphide mineral slurry so that it is not necessary to add carbon, in whatever form, to the slurry nor to control the carbon content in the slurry.

It is apparent from the foregoing description which relates to the general principles of the invention that the supply of oxygen to the slurry is monitored and controlled to provide a desired dissolved oxygen concentration level in the slurry 20. This can be done in a variety of ways e.g. by controlling one or more of the following in an appropriate manner namely: the slurry feed rate, the air flow rate from the source 36, the oxygen flow rate from the source 32, and any variation of the foregoing.

The carbon dioxide flow rate is changed in accordance with the total gas flow rate to the sparger 44 in order to maintain a concentration in the gas phase, i.e. in the gas stream to the reactor, of from 0.5% to 5% carbon dioxide by volume. This carbon dioxide range has been found to maintain an adequate dissolved carbon dioxide concentration in the slurry, a factor which is important in achieving effective leaching.

The addition of oxygen to the sulphide mineral slurry 20 is controlled in order to maintain the minimum dissolved oxygen concentration in solution at a value of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. The upper threshold value depends on the genus and strain of microorganism used in the bioleaching process and typically is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

Figure 1 illustrates the addition of oxygen from a source 32 of pure oxygen. The pure oxygen can be mixed with air from the source 36. Any other suitable gas can be used in place of the air. The addition of oxygen to air results to what is referred to in this specification as oxygen enriched gas i.e. a gas with an oxygen content in excess of 21% by volume. It is possible though to add oxygen substantially in pure form directly to the
5 slurry. As used herein pure oxygen is intended to mean a gas stream which contains more than 85% oxygen by volume.

The temperature in the bioleach reactor or vessel may be controlled in any appropriate way using techniques which are known in the art. In one example the tank 18 is insulated and heating takes place by means of
10 energy which is released by the oxidation of sulphides. The temperature of the slurry 20 is regulated using an internal cooling system 70 which includes a plurality of heat exchanger cooling coils 72 connected to an external heat exchanger 74.

The vessel 18 may be substantially sealed by means of a lid 80. Small vents 82 are provided to allow for the
15 escape of off-gas. The off-gas may, if required, be captured or treated in any appropriate way before being released to atmosphere. Alternatively, according to requirement, the tank 18 may be open to atmosphere.

The microorganisms chosen for the leaching process will determine the leaching temperature, and vice versa. The applicant has found that a preferred operating temperature is above 60°C, for example in the
20 range of 60°C to 85°C. In this range thermophilic microorganisms, in any appropriate combination, are employed. In the range of from 45°C to 60°C, on the other hand, moderate thermophiles are employed while at temperatures below 45°C mesophiles are used. These microorganisms may, for example, be chosen from those referred to hereinbefore.

25 Although the benefit of adding oxygen to the slurry which is to be leached, by making use of oxygen enriched air or, more preferably, by making use of substantially pure oxygen i.e. with an oxygen content in excess of 85%, is most pronounced at high temperatures at which greater leaching rates are possible, a benefit is nonetheless to be seen when oxygen enriched air or substantially pure oxygen is added to the slurry at lower temperatures, of the order of 40°C or even lower. At these temperatures the leaching rates are slower than

at elevated temperatures and although an improvement results from using oxygen enriched air the cost thereof is generally not warranted by the relatively small increase in leaching rate.

Test Results

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The importance of maintaining an adequate supply of oxygen and hence a sufficiently high dissolved oxygen concentration to sustain microorganism growth and mineral oxidation is shown in the results presented in Figure 2. If the dissolved oxygen concentration is allowed to drop below 1.5 ppm, and particularly below 1.0 ppm, biooxidation becomes unstable, which is indicated by higher iron(II) concentrations in solution, of
 10 greater than 2 g/l. At consistent levels of biooxidation, achieved by maintaining a dissolved oxygen concentration above 1.5 ppm, in this experiment, iron(II) is rapidly oxidised to iron(III), and iron(II) concentrations remain generally below 1.0 g/l.

The results presented in Figure 2 were obtained from operation of a first or primary reactor of a continuous
 15 pilot plant treating a chalcopyrite concentrate at a feed solids concentration of 10% by mass and a temperature of 77°C, with *Sulfolobus*-like archaea.

The effect of increasing the oxygen content of the feed gas to a bioreactor and controlling the dissolved oxygen concentration, in accordance with the principles of the invention, was tested in an experiment using a
 20 5m³ bioreactor which was operated with a continuous pyrite or blended pyrrhotite and pyrite flotation concentrate feed, at a temperature of about 77°C, using a mixed culture of *Sulfolobus*-like archaea and a solids density of 10% by mass. The carbon dioxide content in the bioleach inlet gas was controlled at a level of between 1 and 1.5 % by volume. The dissolved oxygen concentration was generally within the range 0.4×10^{-3} kg/m³ to 3.0×10^{-3} kg/m³. The results of the experiment are presented in Figure 3.

25

From the graphs presented in Figure 3 it is clear that, when sparging with air (enriched with carbon dioxide: 20.7% oxygen and 1.0% carbon dioxide), the maximum oxygen demand (directly proportional to the sulphide oxidation duty) was limited to 11.3 kg/m³/day, since the dissolved oxygen concentration which was achievable using air only (i.e. not enriched with oxygen) was just sufficient to maintain microorganism growth.

By controlling the oxygen content of the inlet gas, the oxygen addition rate, and the dissolved oxygen concentration in the slurry in the range of $0.4 \times 10^{-3} \text{ kg/m}^3$ to $3.0 \times 10^{-3} \text{ kg/m}^3$, the oxygen demand, i.e. the sulphide mineral oxidation rate, was increased dramatically. The dissolved oxygen concentration was controlled to a low value, but above the minimum limit for successful microorganism growth, so that the utilisation of oxygen was maximised. The results show the oxygen demand, or sulphide oxidation duty, was increased by over threefold. Thus by increasing the oxygen content in the inlet gas from 20.7% to a maximum of 90.8% the specific oxygen demand was increased from $11.3 \text{ kg/m}^3/\text{day}$ to $33.7 \text{ kg/m}^3/\text{day}$. In addition, by controlling the dissolved oxygen concentration to a low value, but above the minimum value for sustained microorganism growth, the oxygen utilisation was maximised. The oxygen utilisation showed a general increase with an increase in the oxygen content of the inlet gas from 29% (for an inlet gas oxygen content of 20.7%) to 91% (for inlet gas containing 85.5% oxygen).

The high oxygen utilisations achieved of well over 60% are much better than expected. Analysis of the results indicates that the oxygen mass transfer coefficient (M), as defined by equation (1), is significantly and unexpectedly enhanced for operation of the bioreactor at a high temperature (77°C) and with a high oxygen content in the inlet gas (from 29% to 91% in the experiment). In fact, the oxygen mass transfer coefficient (M) is increased by a factor of 2.69, on average, compared to the applicant's design value. This enhancement is after considering the improvement in the mass transfer coefficient due to temperature, which would be expected to increase the value of M by a factor of 1.59 for a temperature increase from 42°C to 77°C , according to the temperature correction factor [proposed by Smith et al ⁽⁵⁾]. This correction factor has been demonstrated experimentally to be valid for a temperature in the range of from 15°C to 70°C .⁽⁶⁾

The determination of the enhanced oxygen mass transfer coefficient is shown from the results presented in Figure 4, where the oxygen demand divided by the design oxygen mass transfer coefficient (M_{design}) is plotted against the oxygen driving force, as defined in equation (1). The slope of the regression line plotted through the data indicates the enhancement in the oxygen mass transfer coefficient by a factor of 2.69.

Process Example

The inventive principles in the preceding section have been described in the context of sulphide minerals in general and, it will be appreciated by those skilled in the art, these principles can be applied in particular to zinc bearing sulphide minerals.

Figure 5 of the accompanying drawings is a process flow chart illustrating the use of the method of the invention for recovering zinc.

In Figure 5 the plant 10 which is shown in Figure 1 and which is described hereinbefore bears the same reference numeral. The oxygen, carbon dioxide and air sources bear the reference numerals 32, 34 and 36 respectively. The zinc bearing sulphide slurry is labelled with the numeral 50.

The slurry 50 is fed to the plant 10 containing one or more bioleach reactors using oxygen enriched gas or pure oxygen, labelled 32, as the oxidant. The oxygen concentration in the reactor is controlled in the manner which has been described hereinbefore depending on the type of microorganism used.

The bioleaching process produces a bioleach residue slurry 100 which contains solubilised zinc and iron, predominantly in the ferric state.

Optionally at this point the bioleach residue slurry 100 may be subjected to a liquid/solid separation step 102 and copper 104, a metal commonly associated with zinc, can be recovered by solvent extraction and electrowinning (106).

Referring again to the main process flow stream iron in the bioleach residue slurry is removed by precipitation (108) brought about by the addition of limestone 110. The resulting slurry 112 is subjected to a liquid/solid separation step 114 producing solids 116 for disposal and a solution 118 which is fed to a zinc solvent extraction step 120. The strip liquor 122 from the solvent extraction step 120 is obtained by stripping the

loaded solvent with spent electrolyte 124 from a subsequent zinc electrowinning step 126 to produce zinc metal cathodes 128.

Optionally raffinate 130 from the solvent extraction step 120 is used as a lixiviant for zinc oxide ore 132 (or concentrate if available) in an oxide leach stage 134. Some limestone 136 may be required to neutralise the acid in the raffinate, to produce gypsum and also to precipitate any co-leached iron and to produce carbon dioxide 140. The limestone will be required if the zinc oxide ore or concentrate 132 is not available.

The oxide leach/acid neutralisation residue is subjected to a liquid/solid separation step 142 to produce solids 144 for disposal and a solution 146 which is fed to the zinc solvent extraction step 120.

A portion of the raffinate 130 may optionally be recycled to the bioleach plant 10 to satisfy the acid requirement in the bioleaching reactor, or it may be directed to an external heap leach 148, where applicable.

If there is insufficient carbonate in the slurry 50 then some of the carbon dioxide 140 generated in the neutralisation step may be added to the slurry, directly, or indirectly, for example by being blended with the oxygen enriched gas 32, or the carbon dioxide from the source 34, to provide the carbon dioxide requirement in the bioleaching phase.

Oxygen gas 150 generated at the anode during the electrowinning step 126 may be recycled to supplement the oxygen requirement during the bioleaching step.

Figure 6 illustrates a variation of the process shown in Figure 5. Steps in the process of Figure 6 which are the same as steps in the process of Figure 5 bear similar reference numerals. The following description relates only to the differences in the processes.

If the solution 118 has a sufficiently high zinc concentration then, instead of using solvent extraction, the solution may be purified by using zinc dust precipitation.

The solution 118 is fed to a purification step 200 in which zinc dust 202 is added to the solution. This causes the precipitation of impurities 204 in accordance with techniques which are known in the art and which consequently are not further described herein.

- 5 The resulting purified solution 206 is fed to the electrowinning step 126. Spent electrolyte 124 is then used in the neutralisation step 134 (instead of the raffinate 130 in Figure 5). The spent electrolyte may also be recycled to the bioleach plant 10 or to the external heap leach 148.

10 The solution 146, in the Figure 6 embodiment, is added to the solution from the solid/liquid separation step 114 to make up the solution 118.

Particular Example

15 Bioleach pilot plant test work was completed, using a sphalerite concentrate assaying 52% zinc, on a pilot plant of approximately 1.1 m³ consisting of 6 reactors configured as 2 primary reactors in parallel followed by 4 secondary reactors in series. The total primary volume was 470l and the total secondary volume was 630l. All test work was carried out at 77°C to 80°C using a zinc bearing sulphide feed slurry containing 7.5% solids. Microorganisms used were a mixed *Sulfolobus*-like archaea. Substantially pure oxygen was fed to the slurry. The oxygen utilisation results obtained in the primary stage during the test work, using analysis of inlet and 20 outlet gas mixtures, are shown in Table 3.

Table 3 : Primary Reactor Zinc Dissolution and Oxygen Uptake Results for Thermophile Pilot Test Work

Retention Days	Zn Dissolution %	Specific Zn Dissolution Rate kg/m ³ /h	Oxygen Uptake (calculated) kg/m ³ /h	Oxygen Uptake (measured) kg/m ³ /h
1.8	90.4	0.865	0.847	0.856
1.5	88.0	1.010	0.989	0.915

The results in Table 3 may be compared to mesophile results obtained at 40°C to 45°C, as reported in the literature⁽⁷⁾. The test work was completed using a sphalerite concentrate containing 48.6% zinc at a similar grind size. The test results are shown in Table 4. Percentage zinc dissolution and oxygen uptakes were not reported, but were calculated using the specific zinc dissolution rate, assuming all zinc was in the form of sphalerite.

Table 4 : Primary Reactor Zinc Dissolution and Oxygen Uptake Results for Mesophile Bioleaching⁽⁷⁾

Solids Content %	Retention Days	Zn Dissolution %	Specific Zn Dissolution Rate kg/m ³ /h	Oxygen Uptake (calculated) kg/m ³ /h
6.7	1.5	55.5	0.42	0.411
12.4	2.1	49.8	0.60	0.587

- 10 The results indicate that the oxygen uptake rate and hence the bioleaching rate may be enhanced by a factor of up to 1.5 to 2 by feeding oxygen enriched air or substantially pure oxygen to the slurry under controlled conditions.

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6/pst

RECOVERY OF ZINC FROM ZINC BEARING SULPHIDE MINERALSBACKGROUND OF THE INVENTION

5 : This invention relates to the recovery of zinc from zinc bearing sulphide minerals.

Commercial bioleach plants which are currently in operation treating sulphide minerals, typically operate within the temperature range of 40°C to 50°C and rely on sparging air to the bioleach reactors to provide the required oxygen. Operation at this relatively low temperature and the use of air to supply oxygen, limit the
10 rate of sulphide mineral oxidation that can be achieved.

The use of high temperatures between 50°C and 100°C greatly increases the rate of sulphide mineral leaching.

15 The solubility of oxygen is however limited at high temperatures and the rate of sulphide mineral leaching becomes limited. In the case of using air for the supply of oxygen, the effect of limited oxygen solubility is such that the rate of sulphide mineral leaching becomes dependent on and is limited by the rate of oxygen transfer from the gas to the liquid phase ^(1,2).

20 The bioleaching of zinc sulphide minerals is similarly problematic and to the applicant's knowledge no commercial zinc bioleaching plant is in operation.

SUMMARY OF THE INVENTION

25 The invention provides a method of recovering zinc from a zinc bearing sulphide mineral slurry which includes the steps of:

- (a) subjecting the slurry to a bioleaching process,
- (b) supplying a feed gas which contains in excess of 21% oxygen by volume, to the slurry, and
- (c) recovering zinc from a bioleach residue of the bioleaching process.

If the slurry contains copper then preferably copper is removed from the bioleach residue before recovering zinc from the slurry.

The method may include the step of removing iron from the bioleach residue before recovering zinc therefrom. This may be done in any appropriate way and preferably the iron is precipitated from the bioleach residue by the addition of limestone to the slurry.

Zinc may be extracted from the residue in any appropriate way. In one form of the invention the bioleach residue is subjected to a recovery process which includes solvent extraction and an electrowinning process to produce zinc metal cathodes.

Oxygen generated during the zinc electrowinning step may be fed to the feed gas of step (b) or directly to the slurry.

Raffinate produced during the solvent extraction step may be supplied to at least one of the following: the bioleaching process of step (a), an external heap leach process, and a zinc oxide leach step.

As used herein "zinc oxide" includes ores or concentrates containing non-sulphide zinc minerals.

Acid in the raffinate may be neutralised to produce gypsum and carbon dioxide and to precipitate any co-leached iron.

The neutralisation may be effected by adding limestone or zinc oxide to the raffinate.

At least some of the carbon dioxide produced during the neutralisation step may be supplied to the bioleaching process of step (a).

As used herein the expression "oxygen enriched gas" is intended to include a gas, e.g. air, which contains in excess of 21% oxygen by volume. This is an oxygen content greater than the oxygen content of air. The expression "pure oxygen" is intended to include a gas which contains in excess of 85% oxygen by volume.

Preferably the feed gas which is supplied to the slurry contains in excess of 85% oxygen by volume i.e. is substantially pure oxygen.

The method may include the step of maintaining the dissolved oxygen concentration in the slurry within a desired range which may be determined by the operating conditions and the type of microorganisms used for leaching. The applicant has established that a lower limit for the dissolved oxygen concentration to sustain microorganism growth and mineral oxidation, is in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. On the other hand if the dissolved oxygen concentration is too high then microorganism growth is inhibited. The upper threshold concentration also depends on the genus and strain of microorganism used in the leaching process and typically is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

Thus, preferably, the dissolved oxygen concentration in the slurry is maintained in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

The method may include the steps of determining the dissolved oxygen concentration in the slurry and, in response thereto, of controlling at least one of the following: the oxygen content of the feed gas, the rate of supply of the feed gas to the slurry, and the rate of feed of slurry to a reactor.

The dissolved oxygen concentration in the slurry may be determined in any appropriate way, e.g. by one or more of the following: by direct measurement of the dissolved oxygen concentration in the slurry, by measurement of the oxygen content in gas above the slurry, and indirectly by measurement of the oxygen content in off-gas from the slurry, taking into account the rate of oxygen supply, whether in gas enriched or pure form, to the slurry, and other relevant factors.

The method may include the step of controlling the carbon content of the slurry. This may be achieved by one or more of the following: the addition of carbon dioxide gas to the slurry, and the addition of other carbonaceous material to the slurry.

- 5 The method may extend to the step of controlling the carbon dioxide content of the feed gas to the slurry in the range of from 0.5% to 5% by volume. A suitable figure is of the order of 1% to 1.5% by volume. The level of the carbon dioxide is chosen to maintain high rates of microorganism growth and sulphide mineral oxidation.
- 10 The bioleaching process is preferably carried out at an elevated temperature. As stated hereinbefore the bioleaching rate increases with an increase in operating temperature. Clearly the microorganisms which are used for bioleaching are determined by the operating temperature and vice versa. As the addition of oxygen enriched gas or substantially pure oxygen to the slurry has a cost factor it is desirable to operate at a temperature which increases the leaching rate by an amount which more than compensates for the increase
- 15 in operating cost. Thus, preferably, the bioleaching is carried out at a temperature in excess of 40°C.

The bioleaching may be carried out at a temperature of up to 100°C or more and preferably is carried out at a temperature which lies in a range of from 60°C to 85°C.

- 20 In one form of the invention the method includes the step of bioleaching the slurry at a temperature of up to 45°C using mesophile microorganisms. These microorganisms may, for example, be selected from the following genus groups:

Acidithiobacillus (formerly *Thiobacillus*); *Leptosprillum*; *Ferromicrobium*; and *Acidiphilium*.

- 25 In order to operate at this temperature the said microorganisms may, for example, be selected from the following species:

Acidithiobacillus caldus (*Thiobacillus caldus*); *Acidithiobacillus thiooxidans* (*Thiobacillus thiooxidans*), *Acidithiobacillus ferrooxidans* (*Thiobacillus ferrooxidans*); *Acidithiobacillus acidophilus* (*Thiobacillus*

acidophilus); *Thiobacillus prosperus*; *Leptospirillum ferrooxidans*, *Ferromicrobium acidophilus*; and *Acidiphilium cryptum*.

If the bioleaching step is carried out at a temperature of from 45°C to 60°C then moderate thermophile
 5 microorganisms may be used. These may, for example, be selected from the following genus groups:
Acidithiobacillus (formerly *Thiobacillus*); *Acidimicrobium*; *Sulfobacillus*; *Ferroplasma* (*Ferriplasma*); and
Alicyclobacillus.

Suitable moderate thermophile microorganisms may, for example, be selected from the following species:
 10 *Acidithiobacillus caldus* (formerly *Thiobacillus caldus*); *Acidimicrobium ferrooxidans*; *Sulfobacillus*
acidophilus; *Sulfobacillus disulfidooxidans*; *Sulfobacillus thermosulfidooxidans*; *Ferroplasma acidarmanus*,
Thermoplasma acidophilum; and *Alicyclobacillus acidocaldrius*.

It is preferred to operate the leaching process at a temperature in the range of from 60°C to 85°C using
 15 thermophilic microorganisms. These may, for example, be selected from the following genus groups:
Acidothermus; *Sulfolobus*; *Metallosphaera*; *Acidianus*; *Ferroplasma* (*Ferriplasma*); *Thermoplasma*; and
Picrophilus.

Suitable thermophilic microorganisms may, for example, be selected from the following species:
 20 *Sulfolobus metallicus*; *Sulfolobus acidocaldarius*; *Sulfolobus thermosulfidooxidans*; *Acidianus infernus*,
Metallosphaera sedula; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; *Thermoplasma volcanium*;
 and *Picrophilus oshimae*.

The slurry may be leached in a reactor tank or vessel which is open to atmosphere or substantially closed. In
 25 the latter case vents for off-gas may be provided from the reactor.

According to a different aspect of the invention there is provided a method of recovering zinc from a slurry
 containing zinc bearing sulphide minerals which includes the steps of bioleaching the slurry using suitable

Preferably the bioleaching is carried out at a temperature in excess of 60°C.

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Preferably the gas contains in excess of 85% oxygen by volume.

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The invention also extends to a method of enhancing the oxygen mass transfer coefficient from a gas phase to a liquid phase in a zinc bearing sulphide slurry which includes the step of supplying a feed gas containing in excess of 21% oxygen by volume to the slurry.

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The oxygen may be supplied to the slurry in the form of oxygen enriched gas or substantially pure oxygen.

The reactor vessel may be operated at a temperature in excess of 60°C and preferably in the range of 60°C to 85°C.

The invention further extends to a method of bioleaching an aqueous slurry containing zinc sulphide minerals which includes the steps of bioleaching the slurry at a temperature above 60°C, and maintaining the dissolved oxygen concentration in the slurry in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

Various techniques may be used for controlling the supply of oxygen to the slurry and hence for controlling the dissolved oxygen concentration in the slurry at a desired value. Use may for example be made of valves which are operated manually. For more accurate control use may be made of an automatic control system. These techniques are known in the art and are not further described herein.

As has been indicated oxygen and carbon dioxide may be added to the slurry in accordance with predetermined criteria. Although the addition of these materials may be based on expected demand and measurement of other performance parameters, such as iron(II) concentration, it is preferred to make use of suitable measurement probes to sample the actual values of the critical parameters.

For example use may be made of a dissolved oxygen probe to measure the dissolved oxygen concentration in the slurry directly. To achieve this the probe is immersed in the slurry. The dissolved oxygen concentration may be measured indirectly by using a probe in the reactor off-gas or by transmitting a sample of the off-gas, at regular intervals, to an oxygen gas analyser. Again it is pointed out that measuring techniques of this type are known in the art and accordingly any appropriate technique can be used.

A preferred approach to the control aspect is to utilise one or more probes to measure the dissolved oxygen concentration in the slurry, whether directly or indirectly. The probes produce one or more control signals which are used to control the operation of a suitable valve or valves, e.g. solenoid valves, automatically so that the supply of oxygen to an air stream which is being fed to the slurry is varied automatically in accordance with real time measurements of the dissolved oxygen concentration in the slurry

Although it is preferred to control the addition of oxygen to a gas stream which is fed to the slurry a reverse approach may be adopted in that the oxygen supply rate to the reactor vessel may be maintained substantially constant and the rate of supply of the sulphide mineral slurry to the reactor vessel may be varied to achieve a desired dissolved oxygen concentration.

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The invention is not limited to the actual control technique employed and is intended to extend to variations of the foregoing approaches and to any equivalent process.

Sphalerite, a commonly occurring zinc sulphide mineral, is of particular benefit, because it has a high leaching rate, even at typical mesophile operating temperatures, which is further increased at the higher temperatures used with moderate and extreme thermophiles. Thus the benefits of the invention, including a high specific reactor sulphide oxidation duty and reduced specific power requirement for oxidation, are obtained during the bioleaching of zinc bearing sulphide concentrates, even at mesophile operating temperatures.

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Bioleaching fixes the sulphur in the sulphide concentrate ultimately as gypsum, rather than as sulphuric acid in conventional processes. Thus there always exists the need to fix sulphur as gypsum. If oxide zinc bearing ore or concentrates are available, they usually have a significant carbonate related gangue acid requirement. The gangue acid requirement can therefore be used to fix sulphur as gypsum, simultaneously solubilising the zinc content, reducing or eliminating the need for additional sulphuric acid for the treatment of these zinc oxide materials. For example a zinc oxide ore with a gangue acid consumption of 200kg sulphuric acid per tonne of ore could be processed using the acid generated from a zinc sulphide bioleach. If only 50% of the zinc oxide ore sulphuric acid requirement were to be met in this way, a 1 million tonnes per annum oxide leach would save US\$5 million per annum at a sulphuric acid price of US\$50 per tonne. The dilute sulphuric acid used for leaching of these zinc oxide materials would come either from a solvent extraction raffinate or from spent electrolyte, depending on the route chosen for zinc recovery.

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Zinc may be recovered from solution by any appropriate process, for example by direct electrowinning, (after purification of the solution by zinc dust precipitation), by solvent extraction or by resin-in-pulp (applied to the slurry), followed by electrowinning.

- 5 If electrowinning is selected as the production method for zinc, the oxygen generated at the anode in the electrowinning process may be used to supplement that used in the bioleach process, reducing the capital and operating costs required for oxygen production.

BRIEF DESCRIPTION OF THE DRAWINGS

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The invention is further described by way of example with reference to the accompanying drawings in which:

Figure 1 is a schematic representation of a portion of a plant in which the invention is carried out,

Figures 2 to 4 show various results and parameters obtained from operating a bioreactor in the manner described herein with reference to Figure 1,

- 15 Figure 5 is a flow chart of a zinc recovery process according to the invention, and

Figure 6 illustrates a variation to the process shown in Figure 5.

DESCRIPTION OF PREFERRED EMBODIMENT

20 General Principles

The limitation of low oxygen solubility during bioleaching, using air, at high temperatures, which in turn limits the rate of reaction, requires enrichment of the air with oxygen i.e. air with an oxygen content greater than 21% by volume, or the use of pure oxygen (defined as being greater than 85% oxygen by volume). The use of oxygen enriched air or pure oxygen overcomes the limited rate of reaction due to oxygen supply constraints, but has two major disadvantages:

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- a) the provision of oxygen enriched air or pure oxygen is expensive and requires a high utilisation (>60%) of the oxygen to warrant the additional expense ⁽³⁾; and

- b) if the oxygen level in solution becomes too high microorganism growth is prevented and sulphide mineral bioleaching stops ⁽⁴⁾.

Therefore, in order to realise the benefits of high rates of sulphide mineral leaching at high temperatures in commercial bioleaching plants, the drawbacks of requiring expensive oxygen and the risk of failure if the dissolved oxygen levels become too high must be overcome.

The bioleaching of sulphide minerals at an elevated temperature results in a high rate of sulphide mineral oxidation, but is dependent on the supply of oxygen and carbon dioxide to maintain high rates of sulphide mineral oxidation and of microorganism growth at adequate rates. The absorption of oxygen and carbon dioxide in the bioleaching reactor is limited, in each case, by the rate of mass transfer from the gas phase into the solution phase. For oxygen the rate of oxygen absorption is defined by equation (1) as follows:

$$R = M. (C^* - C_L) \quad (1)$$

where: R = Oxygen demand as mass (kg) per unit volume (m^3) per unit time(s) ($kg/m^3/s$),

M = Oxygen mass transfer coefficient in reciprocal seconds (s^{-1}),

C^* = Saturated dissolved oxygen concentration as mass (kg) per unit volume (m^3) (kg/m^3),
and

C_L = Dissolved oxygen concentration in solution as mass (kg) per unit volume (m^3) (kg/m^3).

The factor $(C^* - C_L)$ is referred to as the oxygen driving force. A similar equation may be used to describe the rate of carbon dioxide supply to the solution. If the sulphide mineral oxidation rate is increased the oxygen demand increases proportionately. To meet a higher oxygen demand either the oxygen mass transfer coefficient (M) or the oxygen driving force $(C^* - C_L)$ must be increased.

An increase in the oxygen mass transfer coefficient may be achieved by increasing the power input to the bioleach reactor mixer. This improves gas dispersion in the sulphide mineral slurry. With this approach, however, an increase in the oxygen mass transfer coefficient of, for example, 40% requires an increase in the power input to the mixer by a factor of as much as 200%, with a commensurate increase in operating costs.

The oxygen driving force may be increased by increasing the saturated dissolved oxygen concentration C^* and reducing the dissolved oxygen content or concentration C_L .

Microorganism population growth is limited or prevented if the dissolved oxygen concentration C^* reaches too high a level. A concentration level above $4 \times 10^{-3} \text{ kg/m}^3$ has been found to be detrimental to *Sulfolobus*-like strains. Certain *Acidithiobacillus* strains, however, have been found to be tolerant to dissolved oxygen concentrations of up to $10 \times 10^{-3} \text{ kg/m}^3$.

The applicant has established that a lower limit for the dissolved oxygen concentration to sustain microorganism growth and mineral oxidation is in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. Thus, in order to provide an adequate, or optimum, supply of oxygen, the dissolved oxygen content or concentration in the sulphide mineral slurry must be monitored and, where appropriate, the addition of oxygen to the sulphide mineral slurry must be controlled in order to maintain the minimum dissolved oxygen concentration in solution at a value of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$.

On the other hand the dissolved oxygen concentration must not exceed an upper threshold value at which microorganism growth is prevented. It is pointed out that the upper threshold concentration depends on the genus and strain of microorganism used in the bioleaching process. A typical upper threshold value is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

As has been previously indicated the rate of sulphide mineral oxidation, which can be achieved when operating at a relatively low temperature of the order of from 40°C to 55°C , is limited. In order to increase the rate of oxidation it is desirable to make use of thermophiles and to operate at temperatures in excess of 60°C . Any suitable microorganism capable of operating within this temperature range may be used. The optimum operating temperature is dependent on the genus and type of microorganism used. Thus moderate thermophiles of the type *Sulfobacillus* are suitable for operating at a temperature of up to 65°C . Thermophiles of the type *Sulfolobus* are suitable for operating at temperatures of from 60°C to at least 85°C . *Sulfolobus metallicus*, for example, shows optimal growth in the temperature range of from 65°C to 70°C .

The applicant has established that the operation of the bioleaching process, using a gas enriched with oxygen, or pure oxygen, as the oxidant, at elevated temperatures of from 40°C to 85°C:

increases the specific sulphide oxidation duty of the reactor considerably;
 results in an unexpected and significantly enhanced oxygen mass transfer rate;

- 5 increases the oxygen utilisation, providing that the dissolved oxygen concentration is controlled above the point where microorganism growth and mineral oxidation are prevented and below the point at which microorganism growth is inhibited; and
 the overall power required for the oxidation of sulphide minerals is significantly reduced.

- 10 The method of the invention represents a significant improvement compared to a bioleach operation carried out at a temperature of from 40°C to 45°C with air.

The controlled addition of oxygen enriched air or pure oxygen directly into the bioreactor improves the oxygen utilisation efficiency. The oxygen utilisation for a conventional commercial bioleach plant (at least 100m³ in
 15 volume) operating at from 40°C to 45°C with air may be expected to achieve a maximum oxygen utilisation factor of from 40% to 50%. Consequently only 40% to 50% of the total mass of oxygen supplied to the bioleach plant is used to oxidise the sulphide minerals. With the method of the invention the oxygen utilisation is significantly higher, of the order of from 60% to 95%. The higher oxygen utilisation is achieved by controlled oxygen addition and results from the enhanced oxygen mass transfer rate and by operating at low
 20 dissolved oxygen concentrations in the solution phase.

It will be appreciated that although high oxygen demand in bioleach reactors has come about primarily by the use of higher temperatures, rapidly leaching sulphide minerals at temperatures below 60°C, using mesophile or moderate thermophile microorganisms, will have similarly high oxygen demands. The method of the
 25 invention is therefore not restricted to suit thermophiles or extreme thermophiles, but also mesophile and moderate thermophile microorganisms.

Another advantage of using air enriched with oxygen or pure oxygen is that the evaporation losses are reduced, because there is less inert gas removing water vapour from the top of the reactor. This is particularly important in areas where water is scarce or expensive.

- 5 In carrying out the method of the invention the temperature of the slurry in the bioleach vessel or reactor may be controlled in any suitable way known in the art. In one example the bioleach reactor is insulated and heating takes place by means of energy which is released by the oxidation of sulphides. The temperature of the slurry is regulated using any suitable cooling system, for example an internal cooling system.
- 10 Table 1 shows typical data for specific sulphide oxidation duty and oxygen utilisation, when bioleaching with air at 40°C to 45°C, in two commercial bioreactors, Plant A and Plant B respectively, (greater than 100m³ in volume).

Table 1 Commercial Bioreactor Performance Results

Description	Units	Plant A	Plant B
Reactor temperature	°C	42	40
Reactor operating volume	m ³	471	896
Oxygen utilisation	%	37.9	43.6
Typical dissolved oxygen concentration	mg/l	2.5	2.7
Oxygen mass transfer coefficient	s ⁻¹	0.047	0.031
Specific oxygen demand	kg/m ³ /day	21.6	14.8
Specific sulphide oxidation duty	kg/m ³ /day	8.9	5.7
Specific power consumption per kg sulphide oxidised	kWh/kgS ²⁻	1.7	1.8

At low temperatures (40°C – 50°C), with air as the inlet gas, which applies to the results for the commercial reactors, Plant A and Plant B, presented in Table 1, the oxygen utilisations achieved are expected and the oxygen mass transfer coefficients (M) correspond to the applicant's design value. The applicant has

determined that if the method of the invention were to be applied to Plant A, the plant performance would be significantly increased, as indicated by the results presented in Table 2.

Table 2 Predicted Improvement In Commercial Bioreactor Performance

	Units	Plant A – typical operation	Plant A – using the method of the invention
Reactor temperature	°C	42	77
Microbial type strain	-	<i>Acidithiobacillus</i>	<i>Sulfolobus</i>
Inlet gas oxygen content	% by volume	20.9	90.0
Oxygen utilisation	%	37.9	93.0
Typical dissolved oxygen concentration	mg/l	2.5	2.5
Specific oxygen demand	kg/m ³ /day	21.6	59.5
Specific sulphide oxidation duty	kg/m ³ /day	8.9	24.5
Specific power consumption per kg sulphide oxidised	kWh/kgS ²⁻	1.7	1.2

The results clearly show the benefit of the invention in achieving higher rates of reaction by the combination of bioleaching at high temperature, adding oxygen enriched gas and by controlling the dissolved oxygen concentration to a predetermined low level (e.g. $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$). The specific sulphide oxidation duty of the reactor is increased by almost threefold. Clearly the upper dissolved oxygen concentration should not be increased above a value at which microorganism growth is inhibited or stopped.

Even though additional capital for the production of oxygen is required, the savings in reactor and other costs at least offset this additional expense. Additionally, the specific power consumption per kg sulphide oxidised is decreased by approximately one-third. In a plant oxidising 300 tonnes of sulphide per day, the power saving, assuming a power cost of US\$0.05 per kWh, would amount to US\$2.8 million per annum. The high oxygen utilisation and increased specific sulphide oxidation capacity of the reactor represent in combination a considerable improvement over conventional bioleaching practice conducted at lower temperatures, with oxygen supplied by air.

Bioleaching Plant

Figure 1 of the accompanying drawings shows a bioleaching plant 10 in which bioleaching is carried out, in accordance with the principles of the invention.

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The plant 10 includes a bioreactor 12 with an agitator or mixer 14 which is driven by means of a motor and gearbox assembly 16.

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In use a tank or vessel 18 of the reactor contains a sulphide mineral slurry 20. An impeller 22 of the agitator is immersed in the slurry and is used for mixing the slurry in a manner which is known in the art.

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A probe 24 is immersed in the slurry and is used for measuring the dissolved oxygen concentration in the slurry. A second probe 26, inside the tank 18 above the surface level 28 of the slurry, is used for measuring the carbon dioxide content in the gas 30 above the slurry 20.

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An oxygen source 32, a carbon dioxide source 34 and an air source 36 are connected through respective control valves 38, 40 and 42 to a sparging system 44, positioned in a lower zone inside the tank 18, immersed in the slurry 20.

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The probe 24 is used to monitor the dissolved oxygen concentration in the sulphide mineral slurry 20 and provides a control signal to a control device 46. The control device controls the operation of the oxygen supply valve 38 in a manner which is known in the art but in accordance with the principles which are described herein in order to maintain a desired dissolved oxygen concentration in the slurry 20.

The probe 26 measures the carbon dioxide content in the gas above the sulphide mineral slurry 20. The probe 26 provides a control signal to a control device 48 which, in turn, controls the operation of the valve 40 in order to control the addition of carbon dioxide from the source 34 to a gas stream flowing to the sparger 44.

The air flow rate from the source 36 to the sparger 44 is controlled by means of the valve 42. Normally the valve is set to provide a more or less constant flow of air from the source 36 to the sparger and the additions of oxygen and carbon dioxide to the air stream are controlled by the valves 38 and 40 respectively. Although this is a preferred approach to adjusting the oxygen and carbon dioxide contents in the air flow to the sparger other techniques can be adopted. For example it is possible, although with a lower degree of preference, to adjust the air stream flow rate and to mix the adjustable air stream with a steady supply of oxygen and a variable supply of carbon dioxide, or vice versa. Another possibility is to have two separate air stream flows to which are added oxygen and carbon dioxide respectively. Irrespective of the technique which is adopted the objective remains the same, namely to control the additions of oxygen and carbon dioxide to the slurry

Slurry 50 is fed from a slurry feed source 52 through a control valve 54 and through an inlet pipe 56 into the interior of the tank 18. The slurry feed rate may be maintained substantially constant, by appropriate adjustment of the valve 54, to ensure that slurry is supplied to the tank 18 at a rate which sustains an optimum leaching rate. The supplies of air, oxygen and carbon dioxide are then regulated, taking into account the substantially constant slurry feed rate, to achieve a desired dissolved oxygen concentration in the slurry 20 in the tank, and a desired carbon dioxide content in the gas 30 above the slurry. Although this is a preferred approach it is apparent that the slurry feed rate could be adjusted, in response to a signal from the probe 24, to achieve a desired dissolved oxygen concentration in the slurry. In other words the rate of oxygen addition to the slurry may be kept substantially constant and the slurry feed rate may be varied according to requirement.

Another variation which can be adopted is to move the probe 24 from a position at which it is immersed in the slurry to a position designated 24A at which it is located in the gas 30 above the level 28. The probe then measures the oxygen contained in the gas above the slurry i.e. the bioreactor off-gas. The oxygen content in the off-gas can also be used as a measure to control the dissolved oxygen concentration in the slurry, taking any other relevant factors into account.

Conversely it may be possible to move the carbon dioxide probe 26 (provided it is capable of measuring the dissolved carbon dioxide content) from a position at which it is directly exposed to the gas 30 to a position designated 26A at which it is immersed in the slurry in the tank. The signal produced by the probe at the position 26A is then used, via the control device 48, to control the addition of carbon dioxide from the source 34 to the air stream from the source 36.

Although the carbon dioxide source 34, which provides carbon dioxide in gas form, is readily controllable and represents a preferred way of introducing carbon into the slurry 20, it is possible to add suitable carbonate materials to the slurry 50 before feeding the slurry to the reactor. Carbonate material may also be added directly to the sulphide mineral slurry 20 in the reactor. In other cases though there may be sufficient carbonate in the sulphide mineral slurry so that it is not necessary to add carbon, in whatever form, to the slurry nor to control the carbon content in the slurry.

It is apparent from the foregoing description which relates to the general principles of the invention that the supply of oxygen to the slurry is monitored and controlled to provide a desired dissolved oxygen concentration level in the slurry 20. This can be done in a variety of ways e.g. by controlling one or more of the following in an appropriate manner namely: the slurry feed rate, the air flow rate from the source 36, the oxygen flow rate from the source 32, and any variation of the foregoing.

The carbon dioxide flow rate is changed in accordance with the total gas flow rate to the sparger 44 in order to maintain a concentration in the gas phase, i.e. in the gas stream to the reactor, of from 0.5% to 5% carbon dioxide by volume. This carbon dioxide range has been found to maintain an adequate dissolved carbon dioxide concentration in the slurry, a factor which is important in achieving effective leaching.

The addition of oxygen to the sulphide mineral slurry 20 is controlled in order to maintain the minimum dissolved oxygen concentration in solution at a value of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. The upper threshold value depends on the genus and strain of microorganism used in the bioleaching process and typically is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

Figure 1 illustrates the addition of oxygen from a source 32 of pure oxygen. The pure oxygen can be mixed with air from the source 36. Any other suitable gas can be used in place of the air. The addition of oxygen to air results to what is referred to in this specification as oxygen enriched gas i.e. a gas with an oxygen content in excess of 21% by volume. It is possible though to add oxygen substantially in pure form directly to the slurry. As used herein pure oxygen is intended to mean a gas stream which contains more than 85% oxygen by volume.

The temperature in the bioleach reactor or vessel may be controlled in any appropriate way using techniques which are known in the art. In one example the tank 18 is insulated and heating takes place by means of energy which is released by the oxidation of sulphides. The temperature of the slurry 20 is regulated using an internal cooling system 70 which includes a plurality of heat exchanger cooling coils 72 connected to an external heat exchanger 74.

The vessel 18 may be substantially sealed by means of a lid 80. Small vents 82 are provided to allow for the escape of off-gas. The off-gas may, if required, be captured or treated in any appropriate way before being released to atmosphere. Alternatively, according to requirement, the tank 18 may be open to atmosphere.

The microorganisms chosen for the leaching process will determine the leaching temperature, and vice versa. The applicant has found that a preferred operating temperature is above 60°C, for example in the range of 60°C to 85°C. In this range thermophilic microorganisms, in any appropriate combination, are employed. In the range of from 45°C to 60°C, on the other hand, moderate thermophiles are employed while at temperatures below 45°C mesophiles are used. These microorganisms may, for example, be chosen from those referred to hereinbefore.

Although the benefit of adding oxygen to the slurry which is to be leached, by making use of oxygen enriched air or, more preferably, by making use of substantially pure oxygen i.e. with an oxygen content in excess of 85%, is most pronounced at high temperatures at which greater leaching rates are possible, a benefit is nonetheless to be seen when oxygen enriched air or substantially pure oxygen is added to the slurry at lower temperatures, of the order of 40°C or even lower. At these temperatures the leaching rates are slower than

at elevated temperatures and although an improvement results from using oxygen enriched air the cost thereof is generally not warranted by the relatively small increase in leaching rate.

Test Results

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The importance of maintaining an adequate supply of oxygen and hence a sufficiently high dissolved oxygen concentration to sustain microorganism growth and mineral oxidation is shown in the results presented in Figure 2. If the dissolved oxygen concentration is allowed to drop below 1.5 ppm, and particularly below 1.0 ppm, biooxidation becomes unstable, which is indicated by higher iron(II) concentrations in solution, of
 10 greater than 2 g/l. At consistent levels of biooxidation, achieved by maintaining a dissolved oxygen concentration above 1.5 ppm, in this experiment, iron(II) is rapidly oxidised to iron(III), and iron(II) concentrations remain generally below 1.0 g/l.

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The results presented in Figure 2 were obtained from operation of a first or primary reactor of a continuous pilot plant treating a chalcopyrite concentrate at a feed solids concentration of 10% by mass and a temperature of 77°C, with *Sulfolobus*-like archaea.

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The effect of increasing the oxygen content of the feed gas to a bioreactor and controlling the dissolved oxygen concentration, in accordance with the principles of the invention, was tested in an experiment using a 5m³ bioreactor which was operated with a continuous pyrite or blended pyrrhotite and pyrite flotation concentrate feed, at a temperature of about 77°C, using a mixed culture of *Sulfolobus*-like archaea and a solids density of 10% by mass. The carbon dioxide content in the bioleach inlet gas was controlled at a level of between 1 and 1.5 % by volume. The dissolved oxygen concentration was generally within the range 0.4×10^{-3} kg/m³ to 3.0×10^{-3} kg/m³. The results of the experiment are presented in Figure 3.

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From the graphs presented in Figure 3 it is clear that, when sparging with air (enriched with carbon dioxide: 20.7% oxygen and 1.0% carbon dioxide), the maximum oxygen demand (directly proportional to the sulphide oxidation duty) was limited to 11.3 kg/m³/day, since the dissolved oxygen concentration which was achievable using air only (i.e. not enriched with oxygen) was just sufficient to maintain microorganism growth.

By controlling the oxygen content of the inlet gas, the oxygen addition rate, and the dissolved oxygen concentration in the slurry in the range of $0.4 \times 10^{-3} \text{ kg/m}^3$ to $3.0 \times 10^{-3} \text{ kg/m}^3$, the oxygen demand, i.e. the sulphide mineral oxidation rate, was increased dramatically. The dissolved oxygen concentration was controlled to a low value, but above the minimum limit for successful microorganism growth, so that the utilisation of oxygen was maximised. The results show the oxygen demand, or sulphide oxidation duty, was increased by over threefold. Thus by increasing the oxygen content in the inlet gas from 20.7% to a maximum of 90.8% the specific oxygen demand was increased from $11.3 \text{ kg/m}^3/\text{day}$ to $33.7 \text{ kg/m}^3/\text{day}$. In addition, by controlling the dissolved oxygen concentration to a low value, but above the minimum value for sustained microorganism growth, the oxygen utilisation was maximised. The oxygen utilisation showed a general increase with an increase in the oxygen content of the inlet gas from 29% (for an inlet gas oxygen content of 20.7%) to 91% (for inlet gas containing 85.5% oxygen).

The high oxygen utilisations achieved of well over 60% are much better than expected. Analysis of the results indicates that the oxygen mass transfer coefficient (M), as defined by equation (1), is significantly and unexpectedly enhanced for operation of the bioreactor at a high temperature (77°C) and with a high oxygen content in the inlet gas (from 29% to 91% in the experiment). In fact, the oxygen mass transfer coefficient (M) is increased by a factor of 2.69, on average, compared to the applicant's design value. This enhancement is after considering the improvement in the mass transfer coefficient due to temperature, which would be expected to increase the value of M by a factor of 1.59 for a temperature increase from 42°C to 77°C , according to the temperature correction factor proposed by Smith et al ⁽⁵⁾. This correction factor has been demonstrated experimentally to be valid for a temperature in the range of from 15°C to 70°C ⁽⁶⁾.

The determination of the enhanced oxygen mass transfer coefficient is shown from the results presented in Figure 4, where the oxygen demand divided by the design oxygen mass transfer coefficient (M_{design}) is plotted against the oxygen driving force, as defined in equation (1). The slope of the regression line plotted through the data indicates the enhancement in the oxygen mass transfer coefficient by a factor of 2.69.

Process Example

The inventive principles in the preceding section have been described in the context of sulphide minerals in general and, it will be appreciated by those skilled in the art, these principles can be applied in particular to zinc bearing sulphide minerals.

Figure 5 of the accompanying drawings is a process flow chart illustrating the use of the method of the invention for recovering zinc.

In Figure 5 the plant 10 which is shown in Figure 1 and which is described hereinbefore bears the same reference numeral. The oxygen, carbon dioxide and air sources bear the reference numerals 32, 34 and 36 respectively. The zinc bearing sulphide slurry is labelled with the numeral 50.

The slurry 50 is fed to the plant 10 containing one or more bioleach reactors using oxygen enriched gas or pure oxygen, labelled 32, as the oxidant. The oxygen concentration in the reactor is controlled in the manner which has been described hereinbefore depending on the type of microorganism used.

The bioleaching process produces a bioleach residue slurry 100 which contains solubilised zinc and iron, predominantly in the ferric state.

Optionally at this point the bioleach residue slurry 100 may be subjected to a liquid/solid separation step 102 and copper 104, a metal commonly associated with zinc, can be recovered by solvent extraction and electrowinning (106).

Referring again to the main process flow stream iron in the bioleach residue slurry is removed by precipitation (108) brought about by the addition of limestone 110. The resulting slurry 112 is subjected to a liquid/solid separation step 114 producing solids 116 for disposal and a solution 118 which is fed to a zinc solvent extraction step 120. The strip liquor 122 from the solvent extraction step 120 is obtained by stripping the

The solution 118 is fed to a purification step 200 in which zinc dust 202 is added to the solution. This causes the precipitation of impurities 204 in accordance with techniques which are known in the art and which consequently are not further described herein.

- 5 The resulting purified solution 206 is fed to the electrowinning step 126. Spent electrolyte 124 is then used in the neutralisation step 134 (instead of the raffinate 130 in Figure 5). The spent electrolyte may also be recycled to the bioleach plant 10 or to the external heap leach 148.

10 The solution 146, in the Figure 6 embodiment, is added to the solution from the solid/liquid separation step 114 to make up the solution 118.

Particular Example

15 Bioleach pilot plant test work was completed, using a sphalerite concentrate assaying 52% zinc, on a pilot plant of approximately 1.1 m³ consisting of 6 reactors configured as 2 primary reactors in parallel followed by 4 secondary reactors in series. The total primary volume was 470l and the total secondary volume was 630l. All test work was carried out at 77°C to 80°C using a zinc bearing sulphide feed slurry containing 7.5% solids. Microorganisms used were a mixed *Sulfolobus*-like archaea. Substantially pure oxygen was fed to the slurry. The oxygen utilisation results obtained in the primary stage during the test work, using analysis of inlet and 20 outlet gas mixtures, are shown in Table 3.

Table 3 : Primary Reactor Zinc Dissolution and Oxygen Uptake Results for Thermophile Pilot Test Work

Retention Days	Zn Dissolution %	Specific Zn Dissolution Rate kg/m ³ /h	Oxygen Uptake (calculated) kg/m ³ /h	Oxygen Uptake (measured) kg/m ³ /h
1.8	90.4	0.865	0.847	0.856
1.5	88.0	1.010	0.989	0.915

The results in Table 3 may be compared to mesophile results obtained at 40°C to 45°C, as reported in the literature⁷. The test work was completed using a sphalerite concentrate containing 48.6% zinc at a similar grind size. The test results are shown in Table 4. Percentage zinc dissolution and oxygen uptakes were not reported, but were calculated using the specific zinc dissolution rate, assuming all zinc was in the form of sphalerite.

Table 4 : Primary Reactor Zinc Dissolution and Oxygen Uptake Results for Mesophile Bioleaching ⁽⁷⁾

Solids Content %	Retention Days	Zn Dissolution %	Specific Zn Dissolution Rate kg/m ³ /h	Oxygen Uptake (calculated) kg/m ³ /h
6.7	1.5	55.5	0.42	0.411
12.4	2.1	49.8	0.60	0.587

- 10 The results indicate that the oxygen uptake rate and hence the bioleaching rate may be enhanced by a factor of up to 1.5 to 2 by feeding oxygen enriched air or substantially pure oxygen to the slurry under controlled conditions.

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CLAIMS

1. A method of recovering zinc from a zinc bearing sulphide mineral slurry which includes the steps of:
 - (a) subjecting the slurry in a reactor to a bioleaching process at a temperature in excess of 40°C;
 - (b) supplying a feed gas which contains in excess of 21% oxygen by volume, to the slurry;
 - (c) controlling the dissolved oxygen concentration in the slurry at a level of from 0.2×10^{-3} kg/m³ to 10×10^{-3} kg/m³ by controlling at least one of the following: the oxygen content of the feed gas, the supply of feed gas to the slurry; the rate of feed of slurry to the reactor; and
 - (d) recovering zinc from a bioleach residue of the bioleaching process.
2. A method according to claim 1 wherein copper is removed from the bioleach residue before recovering zinc therefrom.
3. A method according to claim 1 or 2 which includes the step of removing iron from the bioleach residue before recovering zinc therefrom.
4. A method according to claim 3 wherein the iron is precipitated from the bioleach residue by the addition of limestone to the residue.
5. A method according to any one of claims 1 to 4 which the bioleach residue is subjected to a recovery process which includes zinc solvent extraction and zinc electrowinning to produce zinc metal cathodes.
6. A method according to claim 5 wherein oxygen generated during the zinc electrowinning is fed to the feed gas of step (b) or directly to the slurry.
7. A method according to claim 5 or 6 wherein raffinate, produced during the zinc solvent extraction, is supplied to at least one of the following: the bioleaching process of step (a), an external heap leach process, and a zinc oxide leach stage.

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8. A method according to any one of claims 5 to 7 wherein acid in raffinate, produced during the zinc solvent extraction, is neutralized to produce gypsum and carbon dioxide, and to precipitate co-leached iron.
- 5 9. A method according to claim 8 wherein the neutralisation is effected by adding limestone or zinc oxide ore or concentrate to the raffinate.
10. A method according to claim 8 or 9 wherein at least some of the carbon dioxide is supplied to the bioleaching process of step (a).
- 10 11. A method according to any one of claims 1 to 4 wherein the bioleach residue is subjected to zinc dust purification by precipitation and electrowinning to produce zinc metal cathodes.
12. A method according to claim 11 wherein spent electrolyte from the zinc electrowinning is supplied to
15 at least one of the following: the bioleaching process of step (a), an external heap leach process, and a zinc oxide leach stage.
13. A method according to claim 11 or 12 wherein oxygen generated during the zinc electrowinning is fed to the feed gas of step (b), or directly to the slurry.
- 20 14. A method according to any one of claims 11 to 13 wherein spent electrolyte, from the zinc electrowinning, is neutralised to produce gypsum and carbon dioxide, and to precipitate co-leached iron.
- 25 15. A method according to claim 14 wherein the neutralisation is effected by adding limestone or zinc oxide ore or concentrate to the spent electrolyte.
16. A method according to claim 14 or 15 wherein at least some of the carbon dioxide is supplied to the bioleaching process of step (a).

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17. A method according to any one of claims 1 to 16 wherein the feed gas in step (b) contains in excess of 85% oxygen by volume.

18. A method according to any one of claims 1 to 17 which includes the step of controlling the carbon content of the slurry.

19. A method according to any one of claims 1 to 18 which includes the step of controlling the carbon dioxide content of the feed gas in the range of from 0.5% to 5.0% by volume.

20. A method according to any one of claims 1 to 19 wherein the bioleaching process is carried out at a temperature in the range of from 40°C to 100°C.

21. A method according to claim 20 wherein the said temperature is in the range of from 60°C to 85°C.

22. A method according to any one of claims 1 to 19 which includes the step of bioleaching the slurry at a temperature of up to 45°C using mesophile microorganisms.

23. A method according to claim 22 wherein the microorganisms are selected from the following genus groups: *Acidithiobacillus*; *Thiobacillus*; *Leptosprillum*; *Ferromicrobium*; and *Acidiphilium*.

24. A method according to claim 22 or 23 wherein the said microorganisms are selected from the following species: *Acidithiobacillus caldus* (*Thiobacillus caldus*); *Acidithiobacillus thiooxidans* (*Thiobacillus thiooxidans*); *Acidithiobacillus ferrooxidans* (*Thiobacillus ferrooxidans*); *Acidithiobacillus acidophilus* (*Thiobacillus acidophilus*); *Thiobacillus prosperus*; *Leptosprillum ferrooxidans*; *Ferromicrobium acidophilus*; and *Acidiphilium cryptum*.

25. A method according to any one of claims 1 to 20 which includes the step of bioleaching the slurry at a temperature of from 45°C to 60°C using moderate thermophile microorganisms.

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26. A method according to claim 25 wherein the microorganisms are selected from the following genus groups: *Acidithiobacillus* (formerly *Thiobacillus*); *Acidimicrobium*; *Sulfobacillus*; *Ferroplasma* (*Ferriplasma*); and *Alicyclobacillus*.

5 27. A method according to claim 25 or 26 wherein the said microorganisms are selected from the following species: *Acidithiobacillus caldus* (formerly *Thiobacillus caldus*); *Acidimicrobium ferrooxidans*; *Sulfobacillus acidophilus*; *Sulfobacillus disulfidooxidans*; *Sulfobacillus thermosulfidooxidans*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; and *Alicyclobacillus acidocaldarius*.

10 28. A method according to claim 21 which includes the step of bioleaching the slurry at a temperature of from 60°C to 85°C using thermophilic microorganisms.

15 29. A method according to claim 28 wherein the microorganisms are selected from the following genus groups: *Acidothermus*; *Sulfolobus*; *Metallosphaera*; *Acidianus*; *Ferroplasma* (*Ferriplasma*); *Thermoplasma*; and *Picrophilus*.

20 30. A method according to claim 28 or 29 wherein the said microorganisms are selected from the following species: *Sulfolobus metallicus*; *Sulfolobus acidocaldarius*; *Sulfolobus thermosulfidooxidans*; *Acidianus infernus*; *Metallosphaera sedula*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; *Thermoplasma volcanium*; and *Picrophilus oshimae*.

25 31. A plant for recovering zinc from a zinc bearing sulphide mineral slurry which includes a reactor vessel, a source which feeds a zinc bearing sulphide mineral slurry to the vessel wherein a bioleaching process is carried out at a temperature in excess of 40°C, an oxygen source which supplies oxygen in the form of oxygen enriched gas or substantially pure oxygen to the slurry, a device which measures the dissolved oxygen concentration in the slurry in the vessel, a control mechanism whereby, in response to the said measure of dissolved oxygen concentration, the supply

Printed: 12-12-2001

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of oxygen from the oxygen source to the slurry is controlled to achieve a dissolved oxygen concentration in the slurry at a level of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$, and a recovery system which recovers zinc from a bioleach residue from the reactor vessel.

- 5 32. A plant according to claim 31 wherein the reactor vessel is operated at a temperature in excess of 60°C .

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NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,
TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

Published:

— *With international search report.*

- (84) **Designated States (regional):** ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

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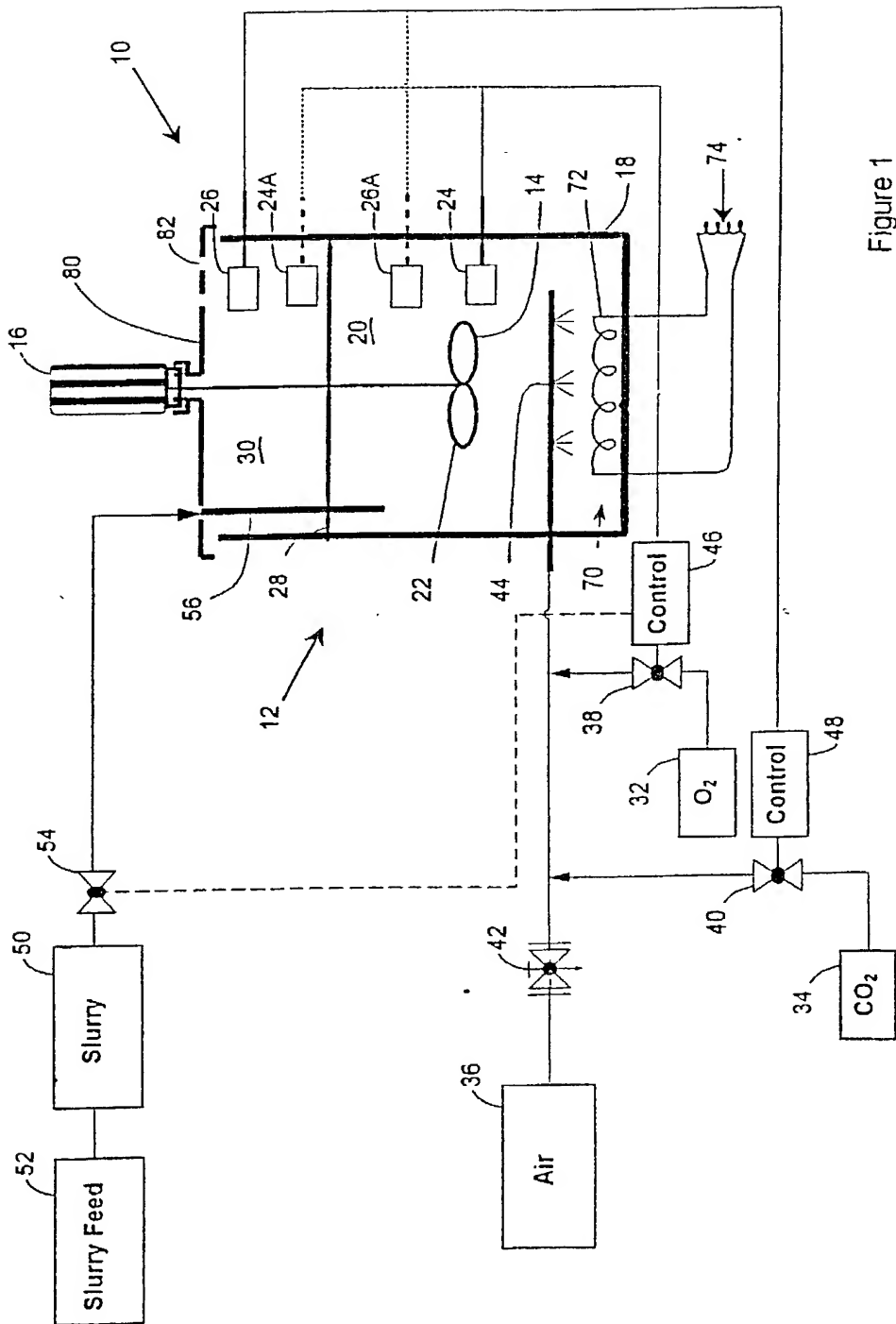


Figure 1

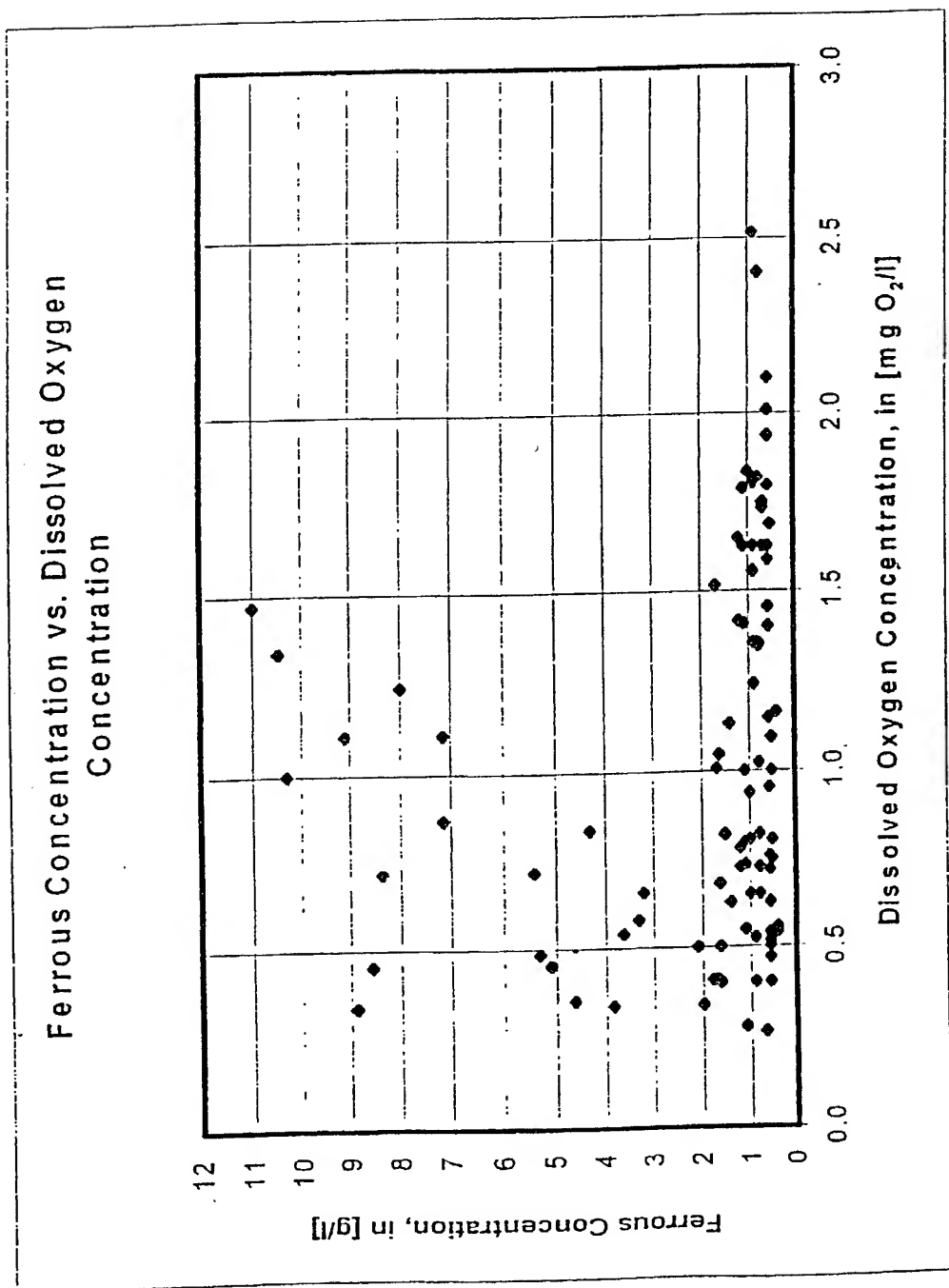


Figure 2 Results Showing The Effect of Reduced Microbial Oxidation On Iron(II) Concentration Levels In Solution As A Result Of Operating At Low Dissolved Oxygen Concentrations

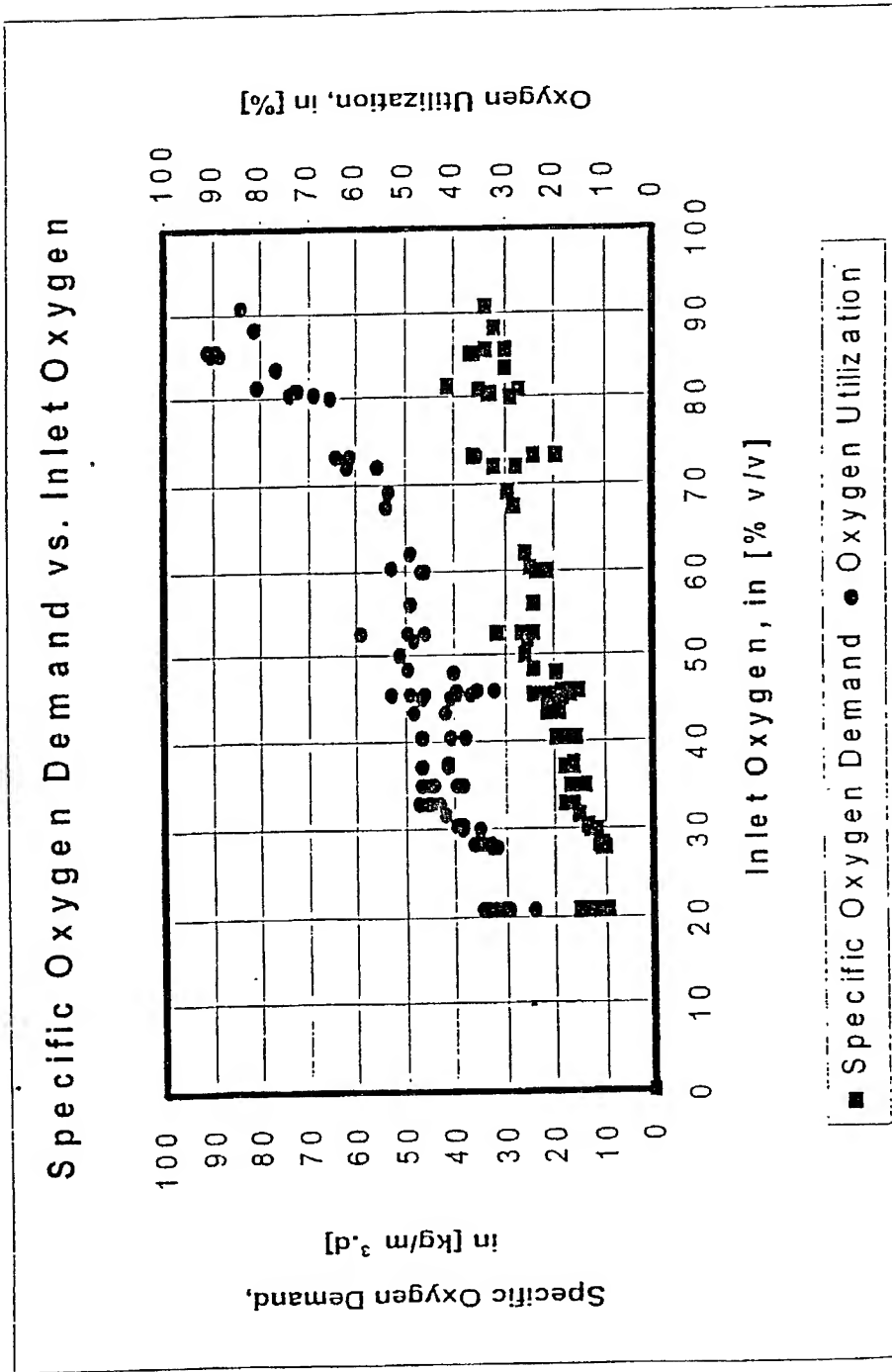


Figure 3 Results Showing The Increase In Specific Oxygen Demand and Oxygen Utilisation Achieved By Increasing The Oxygen Content Of The Inlet Gas Under Controlled Conditions By The Method Of The Invention

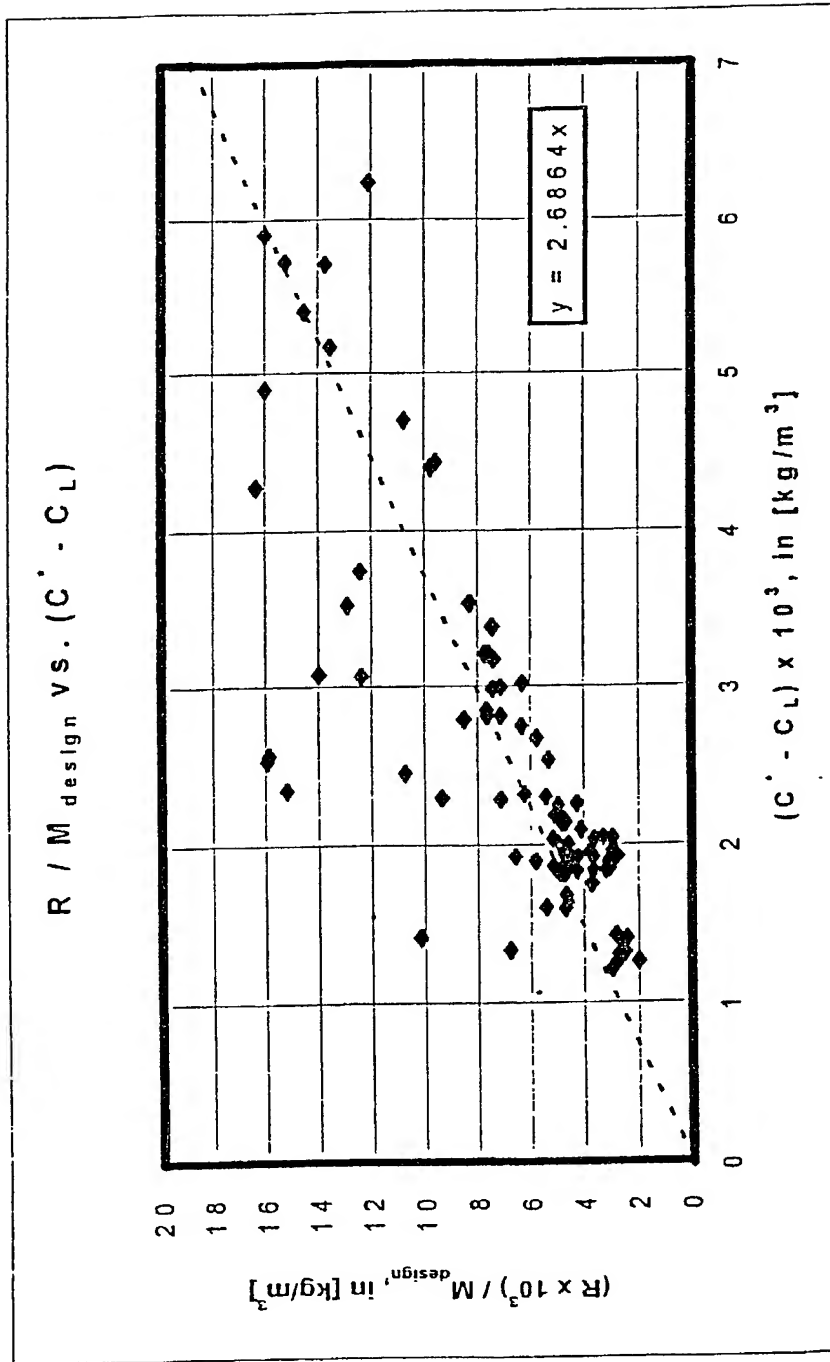


Figure 4 Results Demonstrating The Enhancement Of The Oxygen Mass Transfer Coefficient

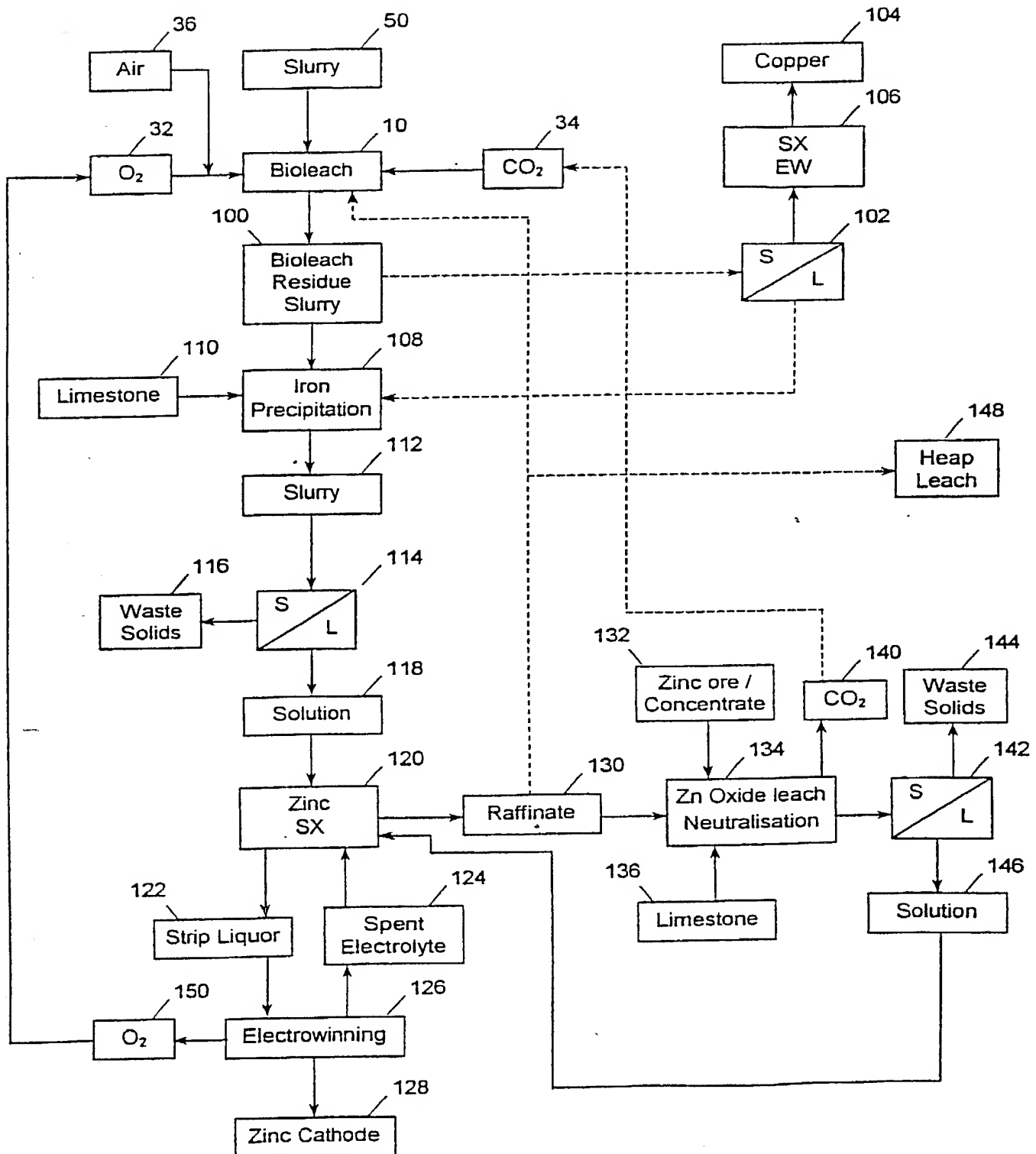


Figure 5

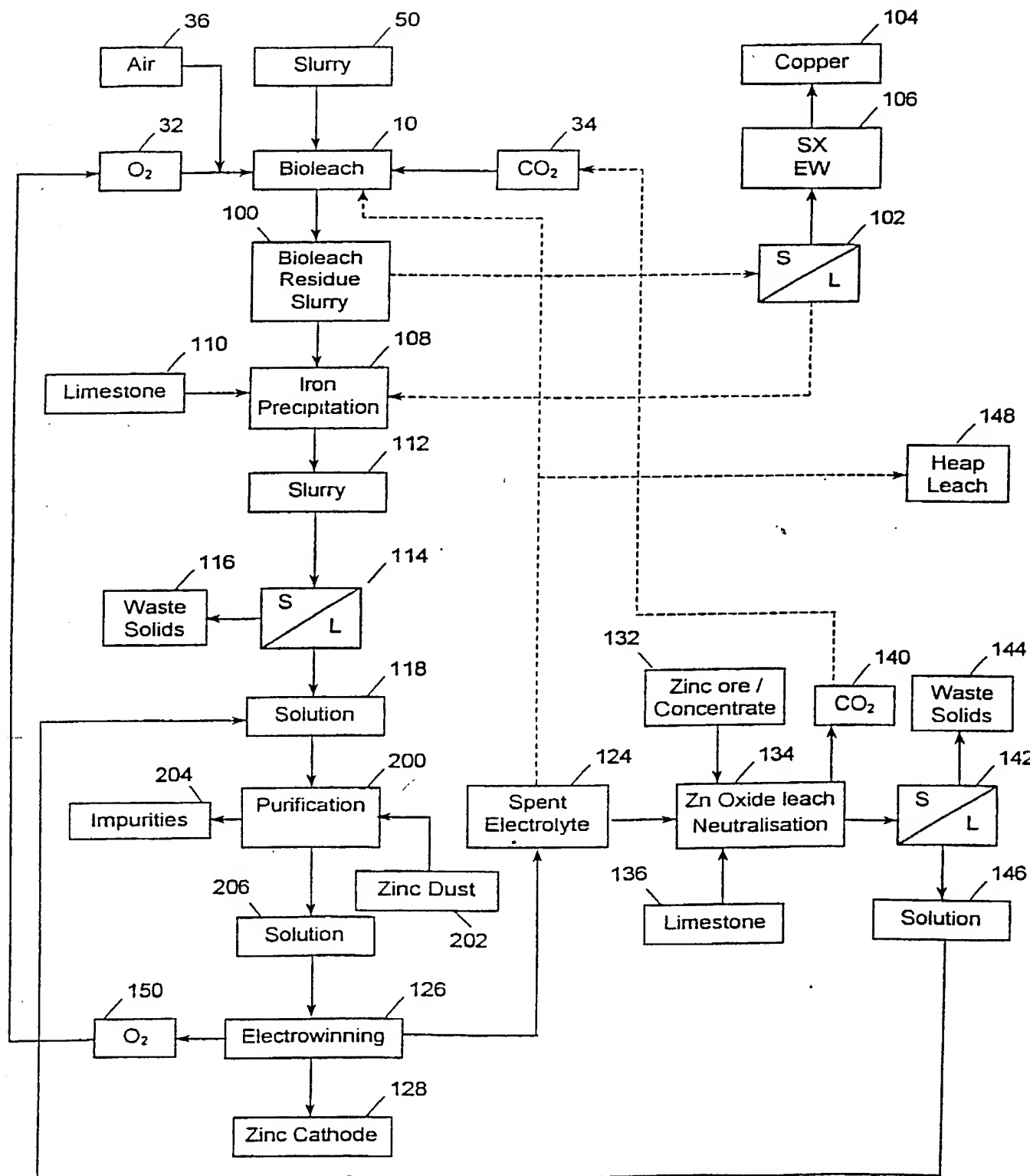


Figure 6

COMBINED DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

This declaration is of the following type:

- ☐ original
- ☐ design
- ☐ supplemental
- ☒ national stage of PCT
- ☐ divisional
- ☐ continuation
- ☐ continuation-in-part (CIP)

My residence, post office address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed for and for which a patent is sought on the invention entitled:

Recovery of Zinc From Zinc Bearing Sulphide Materials by Bioleaching and Electrowinning

the specification of which

- ☐ is attached hereto
- ☐ was filed on _____, as
Application No. _____
and was amended on _____
(if applicable)
- ☒ was described and claimed in PCT International Application No. ZA00/00160
filed on 5 September 2000 and as amended under PCT Article 19 on _____ (if any).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any Amendment referred to above.

I acknowledge duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

- ☐ In compliance with this duty there is attached an Information Disclosure Statement. 37 CFR 1.97.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119, of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent of inventor's certificate having a filing date before that of the application on which priority is claimed:

- ☐ no such applications have been filed
☒ such applications have been filed as follows.

Prior Foreign Application(s)

<u>99/5746</u> (Number)	<u>South Africa</u> (Country)	<u>07 September 1999</u> (day/month/year filed)	<input checked="" type="checkbox"/> <input type="checkbox"/> Yes No
<u> </u> (Number)	<u> </u> (Country)	<u> </u> (day/month/year filed)	<input type="checkbox"/> <input type="checkbox"/> Yes No

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

<u> </u> (Application Number)	<u> </u> (Filing Date)
<u> </u> (Application Number)	<u> </u> (Filing Date)

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below, and insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose all information known to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

<u> </u> (Application No.)	<u> </u> (Filing Date)	<u> </u> (patented, pending, abandoned)
<u> </u> (Application No.)	<u> </u> (Filing Date)	<u> </u> (patented, pending, abandoned)

$$\begin{array}{ccccccc} \frac{\partial^2}{\partial x_1^2} & \frac{\partial^2}{\partial x_1 \partial x_2} & \frac{\partial^2}{\partial x_2^2} & \frac{\partial}{\partial x_1} & \frac{\partial}{\partial x_2} & f \\ 12 D_{xx} & 12 D_{xy} & 12 D_{yy} & 6 D_x & 6 D_y & 0 \end{array}$$

Eric S. Spector, Reg. No. 22,495
Douglas R. Hanscom, Reg. No. 26,600
Jennifer P. Yancy, Reg. No. 47,003

Direct telephone calls to

Jennifer P. Yancy
(703) 415-1500

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100

X

(Date)

ZAX

X South African

200

X church

(Date)

ZAX

X South African

Post Office Address 4 Drakenstein, 52 Outspan Road, Sunset Acres, Johannesburg, 2001.
Republic of South Africa

3-00
Full name of third joint inventor, if any DEW, David William
Inventor's signature X [Signature] 15 March 2002
(Date)
Residence Randburg, Republic of South Africa ZAX
Citizenship X SOUTH AFRICAN
Post Office Address 200 Hans Strijdom Drive, Randburg, 2194, Republic of South Africa

4-00
Full name of fourth joint inventor, if any NORTON, Alan
Inventor's signature X [Signature] 15 March 2002
(Date)
Residence Johannesburg, Republic of South Africa ZAX
Citizenship X BRITISH
Post Office Address 6 Hollard Street, Johannesburg, 2001, Republic of South Africa

Full name of fifth joint inventor, if any _____
Inventor's signature _____ (Date) _____
Residence _____
Citizenship _____
Post Office Address _____